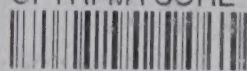


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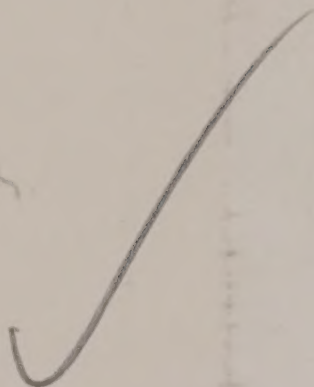
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SIDNEY D. KIRKPATRICK, *Consulting Editor*

INDUSTRIAL STOICHIOMETRY

*Chemical Calculations of
Manufacturing Processes*

McGRAW-HILL SERIES IN CHEMICAL ENGINEERING

SIDNEY D. KIRKPATRICK, *Consulting Editor*

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INDUSTRIAL STOICHIOMETRY

Chemical Calculations of Manufacturing Processes

WARREN K. LEWIS

*Professor Emeritus of Chemical Engineering
Massachusetts Institute of Technology*

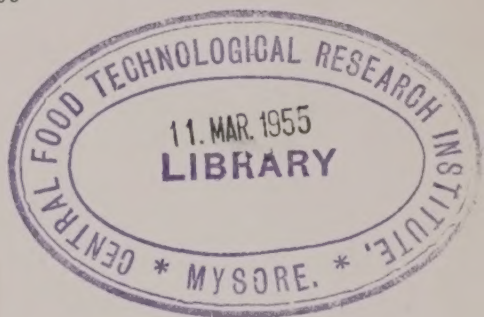
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SECOND EDITION



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Industrial stoic.

To the Memory of
WILLIAM H. WALKER

Pioneer in Chemical Engineering
Whose Teaching Furnished
the Inspiration for This Book

PREFACE

Mastery of the art of using computation methods for quick, effective analysis of process data is an important asset for the technical man in chemical industry. It is particularly valuable for the operating engineer in the interpretation of data taken from plant operations, and for the design engineer in the planning of new equipment and new methods of operation. The principles underlying the methods of computation are unquestioned, but using them is an art, skill in which can be secured only by practice. To introduce the reader to this art this book uses the "case" system—the solution of specific, individual problems, designed not only to show how to manipulate numerical data but to emphasize how quantitative interpretations can develop insight into what is actually going on in an operation or a process. The purpose is to lead the student to an appreciation of the power of "analysis by calculation" as an aid in the work of his profession.

The book is written for two groups of readers, the operating man in the plant and the student beginning the study of chemical technology. The coverage is limited to the inorganic industries because of the relative simplicity of the chemical changes involved and the availability of data. This limitation must not be construed, however, as failure to appreciate the importance of the organic industries.

So far as possible the text is designed to require little or no theoretical preparation beyond that given in a good first-year course in chemistry. This is deemed important because the induction of the student into the art of computation should start at the earliest practicable stage in the curriculum. More chemistry, especially analytical and physical chemistry, is desirable but not essential. While it is not the function of this book to give training in the fundamentals of chemistry, the student's command and appreciation of the science is greatly enhanced by the method of approach here used.

The use of calculus has not been avoided but is incidental to the main line of thought, and the reader unfamiliar with this branch of mathematics will not be significantly handicapped.

Because the ultimate objective is to develop the ability to use stoichiometry in the diagnosis of the performance and the solution of the ills of process operations, problems suitably chosen are unintelligible without an adequate background of familiarity with industrial equipment and processes. The plant man will have this background from his own experience; the student can best use this book in connection with some course in chemical technology in which the teacher makes sure that the background information is properly presented.

It is a mistake, however, to postpone the stoichiometry until presentation of the descriptive material of industrial chemistry is complete. The two should go together. Indeed, the best use of this book will probably be as an auxiliary text for instruction beginning in the sophomore year and continuing through the undergraduate curriculum.

The early chapters are devoted to combustion problems in which the major emphasis is on mechanical techniques of computation. The later chapters on specific chemical industries are designed to illustrate application of these techniques to the interpretation of quantitative data taken from actual plant operations. Chapter 12 can be assigned in connection with a laboratory course in which the student collects experimental data on a chemical process for use as a basis for an approximate design and preliminary economic calculations. The same chapter can be used in plant design courses, and should find use in connection with the parallel activities of industrial practice.

From the start the student should be given an adequate picture of the operation under discussion, though not necessarily of the whole process of which the operation is a part. In the early stages, assignments should be restricted to the more elementary problems at the beginning of each chapter. As time goes on, the student's broadening background and increasing maturity will develop an ever deepening appreciation of the importance of the stoichiometric method in the professional work of the chemical engineer. The more difficult illustrative problems that are found at the ends of the chapters, particularly of the later ones, are specifically chosen with this thought in mind.

The numerical problem method has one serious defect in education for professional work: the student has the problem stated for him, whereas in professional life the engineer must not only formulate the statement for himself, but he himself must first recognize the existence of the problem and collect and evaluate the data for its solution. The text endeavors to stimulate the student to an appreciation of this difficulty as the even treatment goes on, but this phase of instruction is one in which the wise teacher can make a most effective contribution.

It is a quarter of a century since the first edition of this book appeared and the developments of that period, not only in industry itself but also

in educational methods, have made necessary a drastic revision of the original text. Nevertheless, its underlying purpose is unchanged.

For much of the material used we are indebted again and again to contributions from professional colleagues, particularly from associates at Massachusetts Institute of Technology, The Cooper Union, the University of Illinois, and Georgia Institute of Technology. The number of these contributions is so large that individual mention seems out of the question, but our appreciation of their importance is in nowise lessened.

W. K. LEWIS
A. H. RADASCH
H. C. LEWIS

February, 1954

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Chapter 1

INTRODUCTION

The engineer in industry finds himself faced with operations and processes that he must understand thoroughly if he is to control them. It is always possible for him to get by direct observation a considerable body of factual information about a specific situation, but an adequate understanding of the case can never be attained except by a careful and dependable analysis and interpretation of these facts. There are times when an analysis must be purely qualitative in character, but there are other occasions where quantitative interrelationships are so important that no full understanding of the problem can be achieved without a proper study of the numerical data that are or can be made available. In one case it may suffice to prove only that one stream of material in a process is hotter than another stream, with the consequence that heat is being transferred from the first stream to the second and not in the reverse direction. This qualitative result alone may be most important. In another case, such as the burning of sulfur with air to form sulfur dioxide, sulfur trioxide, and ultimately sulfuric acid, it may be necessary to follow the course of oxidation and conversion throughout the equipment. To obtain this information will require several gas and liquor analyses and temperature measurements. The analytical data must be checked for consistency and dependability and must be further examined in the light of equilibrium relationships and heat effects of the chemical reactions involved. Only by a careful and exhaustive analysis of this nature can the process be fully understood.

The purpose of this book is to introduce the reader to the techniques of analysis and interpretation of technical information available on industrial processes involving chemical reactions, with particular emphasis on the use of quantitative methods. It will be shown that the methods are equally applicable to the development and design of new processes, operations, and equipment.

Principles used in chemical calculations. The factors that are by far the most important to the chemical engineer in the interpretation of process data are the fundamental principles of chemical science. It

is a fortunate fact that the most useful of these principles can be grouped under four major headings. Moreover, experience has demonstrated that, when analyzing a specific problem, it is almost always advantageous to take up these groups of principles in a given order, so that adherence to this order is strongly recommended as a rule of procedure. These fundamental groups of principles, in the order recommended for applying them, are as follows:

1. *The law of conservation of matter*, particularly of the elements, together with the laws of chemical combining weights and proportions. These are the laws involved in the ordinary interpretation of the mass (or weight) relationships indicated by chemical reaction equations as conventionally written.

2. *The law of conservation of energy*. In chemical processes this requires allowance for the heat effects of all chemical reactions involved, in addition to all physical-energy effects (heat losses, work effects, and the like) that are associated with the operation.

3. *The equilibrium relationships of the system*. These require an adequate knowledge of the equilibria, both physical and chemical, of all reactions or interactions that actually go on in the system under consideration.

4. *The reaction-rate relationships of the system*. These must include the rates of all changes occurring, whether physical or chemical in character.

Applications of principles to specific problems. It is obvious that a complete understanding of these principles and mastery of the art of using them in specific situations go far indeed toward furnishing the professional equipment of the chemical engineer. Their complexity may tend to discourage the beginner. However, it is possible for him to become thoroughly familiar with the first group of principles without being confused by involvement with the later ones and to follow this by taking up the later principles in order. This procedure has been adopted in the presentation of material in this book, which will put its major emphasis on the first two groups or principles. However, problems of equilibria and, later, certain elementary problems of rate will be taken up. Neither of these last two groups of principles will be treated exhaustively, but consideration will be given to the way in which the principles of conservation of the elements and of energy contribute toward the analysis of equilibrium and rate relationships.

There is another important justification for adhering to the order recommended. The various principles enumerated differ widely in the dependability of their quantitative formulations, and dependability decreases in the order given. The laws of chemical combining weights are valid to an accuracy far beyond that of most experimental measure-

ments of mass (weight).¹ This validity is unimpaired by the widest variations in concentration, pressure, temperature, and other conditions of operation. On an absolute basis, the law of conservation of energy is equally valid, but from a practical angle its application loses accuracy because of variations of such factors as pressure, because pressure can profoundly influence the heat effects of a chemical reaction. Thus, the energy content of a gaseous phase can be changed greatly by pressure, owing to energy effects associated with deviations from the gas laws. In a solution, the energy content may be widely different from the sum of the energy contents of its components, even though these be in liquid form. Knowledge of the extent of these deviations and consequently of the exact magnitude of the energy effects is often seriously limited, so that energy calculations may, under specific conditions, be of relatively low dependability. Similarly, knowledge of the effects of pressure and concentration on both chemical and physical equilibria is so limited that quantitative computations may be in serious error, particularly where exhaustive experimental data on the effects of such factors are not available. Finally, knowledge of reaction-rate relationships is in such an elementary state that in few cases are quantitative estimates dependable to better than a few per cent and in many cases they represent only crude approximations. It is obviously preferable to carry out first those phases of computation concerning the dependability of which there is least doubt, leaving to a later stage the steps of calculation that have the least dependable bases.

Sometimes a problem may be encountered in which element balances throw no significant light on the situation. In that case, the thing to do is to go on to the energy relationships. If data are not available for handling these, they too may be passed over, leaving an analysis of the equilibria as the next step to take. However, the common problems of industry are not of this sort, and it is recommended that in each case the attempt be made to apply each group of principles in the order given above, endeavoring to exhaust the potentialities of analysis under each before proceeding to the next. Sometimes it will be necessary to back-track because information developed by calculations of equilibria and rate may make it possible to reappraise or carry further element or material balances. In general, however, adherence to the recommended

¹ The ordinary form of the law of conservation of the elements must, of course, be modified when dealing with radioactive elements, but even in this case the correction is usually negligible, except when dealing with such elements of relatively short life. Furthermore, when dealing with isotopes, the proper atomic weights must be used. Obviously, however, in the overwhelming majority of industrial problems no such qualifications come into consideration.

order of steps of computation will be found justifiable and timesaving in the long run.

Illustrative problems. In succeeding chapters the art of applying the above approach is illustrated by a succession of problems whose solutions are presented in the text. For the sake of simplicity, the earlier problems are apt to be artificial in character. However, problems consisting of actual cases drawn from the technical literature and from the industrial experience of the authors are introduced at an early stage, and the bulk of the material is of this character.

Since the illustrative problems form most of the text, the way in which they are read is important. If the student will pause after finishing the statement of each problem and take the time to think through to what method of attack he would adopt if he actually had to solve the problem on his own, then as he reads the printed solution he can distinguish between the points he could have handled by himself and those he would have missed if on his own. The latter, of course, are the ones to study.

Certain elementary concepts of physics and chemistry are so often used that it is advisable to review them at this point to make certain that a ready understanding of them may be counted on as part of the reader's equipment for analyzing and interpreting the data of industrial processes.

Molal units. As in analytical and physical chemistry, so in industrial stoichiometry, it is frequently advantageous to use the *mol* as the unit of quantity. Whereas in scientific work the gram mol (*i.e.*, a mass in grams equal to the molecular weight of the substance in question) is employed almost exclusively, in industrial work the pound mol (a mass in pounds equal to the molecular weight of the material) is often more convenient. Where any doubt exists as to molecular weight, as, for example, with materials subject to partial dissociation, polymerization, or the like, the value of the molecular weight employed must be clearly indicated. Frequently, the gram atom or pound atom is also used, and it is sometimes loosely referred to as "mol." Since there are 454 grams in a pound, it follows that a pound mol is 454 gram mols, but as will appear later, this relationship is seldom used.

Gas laws. The behavior of the so-called "perfect gases" is indicated by the equation

$$pv = nRT$$

In this equation p is the absolute pressure of the gas, v its volume, n the number of mols of the gas under consideration, R the gas constant, and T the absolute temperature.

Both pressure and volume can be in any units desired and the temperature on any scale, but the scale must start at the absolute zero.

Since the absolute zero of temperature is approximately -273°C , *i.e.*, -460°F , then 273 must be added to the centigrade temperature and 460 to the Fahrenheit temperature to get the respective absolute temperatures. Absolute temperatures on the centigrade scale are called degrees Kelvin ($^{\circ}\text{K}$) and on the Fahrenheit scale, degrees Rankine ($^{\circ}\text{R}^*$). The quantity of the gas in mols can also be expressed in any units, but only the gram mol, kilogram mol, and pound mol are ordinarily employed.

The gas constant R is the same for all gases that follow the ideal-gas law, but its numerical value depends on the units in which the other quantities in the equation are expressed. Commonly used values of R are given in Table 1-1.

TABLE 1-1. VALUES OF THE GAS CONSTANT R IN THE EQUATION $pv = nRT$ FOR IDEAL GASES

p	v	n	T	R
atm	liters	g mols	$^{\circ}\text{C abs} = ^{\circ}\text{K}$	$0.08206 \frac{\text{l-atm}}{\text{g mol} \cdot ^{\circ}\text{K}}$
$\frac{\text{lb}}{\text{sq ft}}$	cu ft	lb mols	$^{\circ}\text{F abs} = ^{\circ}\text{R}$	$1543 \frac{\text{ft-lb}}{\text{lb mol} \cdot ^{\circ}\text{R}}$
atm	cu ft	lb mols	$^{\circ}\text{F abs} = ^{\circ}\text{R}$	$0.729 \frac{\text{cu ft-atm}}{\text{lb mol} \cdot ^{\circ}\text{R}}$

Deviations from perfect-gas behavior. The perfect-gas equation gives with good accuracy the relationship between p , v , n , and T for most gases when the pressure is low and the temperature is well above the critical temperature of the gas in question. Thus, for the so-called "permanent gases" at normal and higher temperatures, the deviations from the equation are slight up to several atmospheres and negligible at 1 atm or less. At pressures below atmospheric the deviations of other gases and even of saturated vapors seldom exceed 2 or 3%. As the pressure approaches zero, all gases conform to the equation, regardless of the temperature.

For many gases, however, there are conditions of temperature and pressure where deviations from the perfect-gas law are large and may run to several hundred per cent. The deviations are specific for each gas, or gas mixture, and for exact work they must be determined experimentally. "Equations of state" have been developed for many gases that correlate p - v - T data with considerable exactness, but generally these are too cumbersome to use in most engineering calculations. The most common and convenient method of taking these deviations into

* The error that is most commonly made when converting Fahrenheit temperatures to the corresponding absolute scale is that of failing to remember that while the melting point of ice is 0°C (273°K), it is 32°F (492°R).

account is by the use of a correction factor, called the compressibility factor z , to be used in the equation $pv = znRT$. For many gases the specific values for z , based on direct experimental determinations, are available in tabular or graphical form in the literature. Fortunately for engineering work, there exists for most pure gases a general relationship showing z as a function of temperature and pressure if these are expressed in terms of the so-called "reduced temperature" T_R and "reduced pressure" p_R of the gas in question. These are defined by

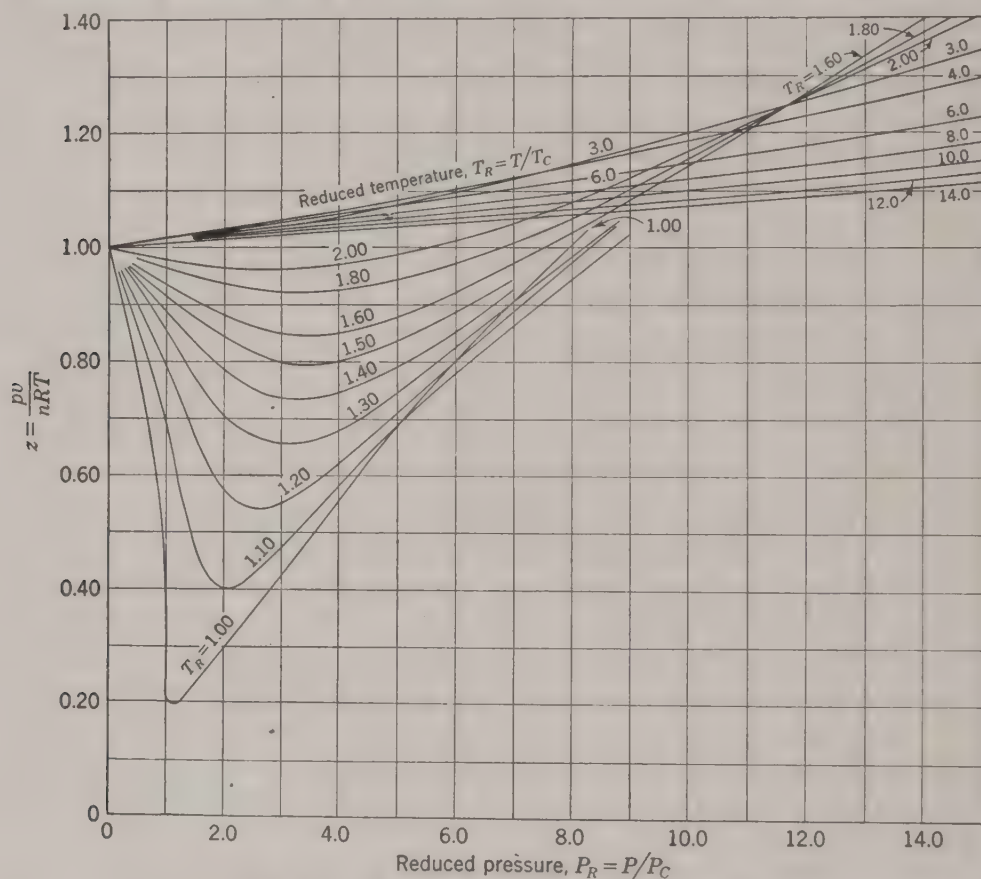


FIG. 1-1. Compressibility factor z for gases.

$T_R = T/T_c$ and $p_R = p/p_c$, where T_c and p_c are respectively the critical temperature and critical pressure of the specific gas.

Figure 1-1, based on the behavior of hydrocarbons, shows the relationship between z , p_R , and T_R . It shows at a glance how real gases differ from ideal gases. For values of p_R below about 8, and for T_R not more than 2, values of z are generally below 1.0; *i.e.*, the pv product, or the actual volume of a gas at a specific pressure, is less—sometimes much less—than would be calculated from $pv = nRT$. Above $p_R = 8$, the opposite is true.

The basic idea underlying a graph like Fig. 1-1 is expressed by the "law of corresponding states," which says that all gases behave alike when in "corresponding states," *i.e.*, when their pressures and temperatures bear given ratios to the critical values. This law in turn is subject to limitations, as is the perfect-gas law. Compressibility factors from Fig. 1-1 will not give the *exact* relationship between p , v , and T for *all* gases under *all* conditions, although these factors can be used where the perfect-gas equation is of little value. For most gases the deviations are not large, usually under 10% in the extreme, whereas the perfect-gas equation might show a deviation as much as 500%. In consequence the chart is extremely useful for engineering estimates. It breaks down for vapors exhibiting molecular association or dissociation, such as acetic acid, phosphorus pentachloride, or elementary sulfur, and for helium and hydrogen. For the last two it can be used when their reduced pressures and temperatures are based, not on their true critical constants, but on $p'_c = 3.26$ atm and $T'_c = 6.3^\circ\text{K}$ for helium, and on $p'_c = 20.8$ atm and $T'_c = 41.3^\circ\text{K}$ for hydrogen.

Gas-law calculations. The following simple examples are given to review the foregoing principles by means of numerical illustrations.

Consider a steel tank having a volumetric capacity of 42 cu ft that contains compressed air at 15 psig (lb/sq in. gauge pressure). The temperature is 72°F . How many pounds of air does the tank contain?

One must first get the total, or absolute, pressure of the air. Since the barometric pressure is not given, this will be assumed to be "normal," *i.e.*, 14.7 lb/sq in., giving for the pressure of the air $15 + 14.7 = 29.7$ psia (lb/sq in. abs). T in degrees Rankine is $460 + 72 = 532$. Then, from $p_v = nRT$,

$$n = \frac{pv}{RT} = \frac{(29.7)(144)(42)}{(1543)(532)} = 0.2185 \text{ mol air}$$

Since the average molecular weight of air is 29.0,

$$0.2185 \times 29.0 = 6.35 \text{ lb air}$$

As an example of the use of the compressibility factor, suppose it is desired to find the volume of 1 lb of methane gas at 0°C and 100 atm pressure. T_c for methane is -82.5°C , and p_c is 45.8 atm.* Thus, T_R for the given conditions is $273/(273 - 82.5) = 1.43$, and

$$p_R = \frac{100}{45.8} = 2.18$$

* Values for the critical constants of a number of substances may be found in the Appendix. Others are to be found in the literature. For example, see J. H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., p. 204, McGraw-Hill Book Co., Inc., New York, 1950; also N. A. Lange and G. M. Forker, "Handbook of Chemistry," 7th ed., pp. 1441-1476, 1502-1503, Handbook Publishers, Inc., Sandusky, Ohio, 1949.

From Fig. 1-1, z is found by interpolation to be 0.785. The volume of 1 lb of methane is then found as follows:

$$\begin{aligned}v &= znRT/p \\n &= (1/16.04) \text{ lb mol} \quad T = 492^\circ\text{R} \\p &= 100 \text{ atm} \quad R = 0.729 \text{ cu ft-atm/lb mol-}^\circ\text{R} \\v &= \frac{(0.785)(1/16.04)(0.729)(492)}{100} = 0.176 \text{ cu ft}\end{aligned}$$

From experimentally determined values of the compressibility factor for methane the volume is 0.175 cu ft. Thus, use of Fig. 1-1, which gives a general relationship between z and reduced temperatures and pressures, gives a value for the volume that, in this case, is 0.6% too high. This good agreement might have been expected, since the figure is based on data for hydrocarbons. On the other hand, if the perfect-gas equation had been used to calculate the volume, the result would have been 27.5% too high.

As a second example, calculate the volume of 1 lb of hydrogen at -50°C and 200 atm pressure. As was explained above, pseudocritical constants must be used if z for hydrogen is to be obtained from Fig. 1-1. These are $T'_c = 41.3^\circ\text{K}$ and $p'_c = 20.8 \text{ atm}$, giving $T_R = (273 - 50)/41.3 = 5.4$, and $p_R = 200/20.8 = 9.6$, whence $z = 1.15$.

$$\begin{aligned}v &= znRT/p \\n &= (1/2.016) \text{ lb mol} \quad T = 223^\circ\text{K, i.e., } 402^\circ\text{R} \\p &= 200 \text{ atm} \quad R = 0.729 \text{ cu ft-atm/lb mol-}^\circ\text{R} \\v &= \frac{(1.15)(1/2.016)(0.729)(402)}{200} = 0.839 \text{ cu ft}\end{aligned}$$

The experimentally determined volume is 0.840 cu ft. However, the perfect-gas equation would give 0.728 cu ft, a value that is 13.4% too low.

Pound-molecular volume. Pressure and temperature are easily measured, but the volume of a gas is not readily found except by the use of special equipment, and then measurement is, in many cases, entirely impractical on account of the large volumes involved. Hence, the most frequent use of the gas laws is to calculate the volume of a gas when its quantity in mols, or pounds, and its temperature and pressure are known.

Instead of solving the perfect-gas equation for the gas volume, it is often simpler to find the volume under some standard conditions of temperature and pressure and then to correct this standard volume by multiplying by temperature and pressure ratios. This is the method frequently employed in the solution of problems in analytical and physical chemistry, where it is convenient to use the gas laws in terms of the gram-molecular volume. This is the volume, 22.4 liters, of 1 g mol of an

ideal gas under standard conditions (s.c.) of temperature and pressure, which are 0°C and 1 atm. Similarly, in industrial work, it is desirable to use the pound-molecular volume, which is 359 cu ft at 32°F and 1 atm.* Indeed, it is frequently convenient to define the molecular weight of a gas (or of a gas mixture) as the mass in pounds of 359 cu ft of gas, measured at standard conditions.

If the equation for the gas under any conditions is written as $pv = nRT$, and the equation for 1 mol of gas under standard conditions as $p_0v_0 = RT_0$, dividing the first equation by the second and solving for v gives

$$v = n \times v_0 \times \frac{p_0}{p} \times \frac{T}{T_0}$$

That is, the volume in cubic feet equals the number of pound mols times the pound-molecular volume, 359 cu ft, times correction factors for temperature and pressure. Since p_0/p and T/T_0 are ratios, they may be expressed in any units for absolute pressure and temperature as long as the units are the same in any one ratio.

Instead of memorizing the preceding equation, it is well to remember only that the volume at standard conditions must be multiplied by an absolute-temperature ratio and an absolute-pressure ratio and to rely on common sense to determine whether these ratios should be greater or less than unity, according as the gas volume is desired at a higher temperature or lower pressure than standard, or vice versa. Obviously, the same reasoning applies to the conversion of a gas volume from its volume at any conditions not standard by use of the proper pressure and temperature ratios.

The preceding concepts are simple to apply. For example, what is the volume of 100 lb of a gas with an average molecular weight of 18 if it is held at 20 psig and at 100°F?

$$\begin{aligned} v &= n \times 359 \times \frac{p_0}{p} \times \frac{T}{T_0} \\ n &= \frac{100}{18} \\ \frac{p_0}{p} &= \frac{14.7}{(14.7 + 20)} \\ \frac{T}{T_0} &= \frac{(460 + 100)}{492} \end{aligned}$$

* In the manufactured-gas industry it is standard practice to report gas volumes in cubic feet at 30 in. Hg absolute pressure, and at 60°F, saturated with water vapor. Calculations, however, are made on the basis of dry gas at 30 in. Hg and 60°F, under which conditions the pound-molecular volume is 378 cu ft. The saturated volume, *i.e.*, the volume of 1 mol of dry gas after saturation with water vapor, is 385 cu ft.

In the natural-gas industry several standards are encountered, but the one most frequently used is dry gas at 60°F and 1 atm.

Note that the pressure ratio is less than unity because the gas is at a higher pressure than atmospheric and therefore has a lesser volume than it has at standard conditions. Note also that the temperature ratio is greater than unity because of the higher temperature.

$$v = \left(\frac{100}{18}\right) (359) \left(\frac{14.7}{34.7}\right) \left(\frac{560}{492}\right) = 961 \text{ cu ft}$$

Dalton's law of partial pressures. Another law applicable to gas mixtures at low pressures is Dalton's law relative to the additivity of partial pressures. It is easily seen that in any mixture of gases the components of which follow the gas laws, the volume per cent of any component is equal to the mol per cent of that component and is also equal to the partial pressure of that component expressed as a percentage of the total pressure. This may be written:

$$\text{Volume per cent} = 100 (\text{mol fraction}) = 100 \frac{\text{partial pressure}}{\text{total pressure}}$$

This rule is used in all volumetric gas analyses which are made at atmospheric pressure or below. In general, the partial pressures of the individual components are so low that the deviations from the gas laws are less than the manipulative errors of analysis. However, should conditions where this is not the case be encountered, analysis must be made by other methods or else the results corrected for the deviations. It is, however, perfectly allowable to make gas analyses at low pressures where the gas laws hold, and then to use the analytical results under higher pressures and lower temperatures where the deviations may be very large, since a change in temperature or pressure alone cannot possibly produce a change in the composition of a mixture as a whole.

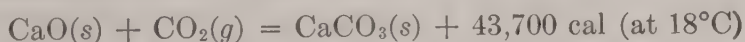
Heat quantities. All the commonly used units of heat energy are defined in terms of the amount of heat required to raise 1 unit mass of water 1 degree in temperature. Thus, in the metric system, the unit of heat is the gram calorie (cal), which is the amount of heat necessary to raise the temperature of 1 g of water 1 centigrade degree.* In the English system it is the British thermal unit (Btu), which is the heat required to raise the temperature of 1 lb of water 1 Fahrenheit degree. Another unit is the centigrade heat unit (Chu), which is the heat necessary to raise 1 lb of water 1 centigrade degree. The centigrade heat unit mixes units from the two systems, but for that very reason it is convenient to use in many thermal calculations because of the ease of applying thermal data from the scientific literature to industrial calculations and because many chemical plants which measure their materials in pounds employ the centigrade temperature scale in their manufacturing operations.

* The exact definition specifies the temperature interval to be between 15° and 16°C.

The relationship between any two of these heat quantities is easily seen by referring to the definitions. Since $1 \text{ lb} = 454 \text{ g}$, $1 \text{ Chu} = 454 \text{ cal}$; and since $1 \text{ centigrade degree} = 1.8 \text{ Fahrenheit degrees}$, $1 \text{ Chu} = 1.8 \text{ Btu}$. The relationship between cal and Btu is $1 \text{ Btu} = (454/1.8) \text{ cal} = 252 \text{ cal}$. The first and third of these relationships are seldom used, as will appear from the following discussion and from later problems. It is only necessary to remember that $1 \text{ Chu} = 1.8 \text{ Btu}$, which is simply the relationship between the two temperature scales.

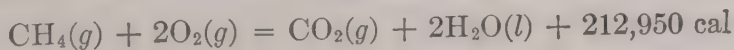
In most chemical calculations the thing of interest is the ratio of the quantity of heat to the quantity of material under consideration. If this ratio has been established in the metric system as $x \text{ cal/g}$, then the ratio must also be $x \text{ Chu/lb}$, where x has the same numerical value in both ratios. This can be seen from the fact that if both numerator and denominator of the first ratio, $x \text{ cal/g}$, are multiplied by 454, then the second ratio, $x \text{ Chu/lb}$, is obtained without change in the value for x . Thus, the statement that a certain liquid has a heat of vaporization of 120 cal/g means that it requires 120 cal to evaporate 1 g and that it will require 120 Chu to evaporate 1 lb .

Heats of reaction. Heats of chemical reactions are almost always given on a molal basis, corresponding to the chemical equation as written in connection therewith. The equation

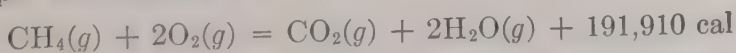


means that 1 mol (56 g) of solid CaO combines with 1 mol (44 g) of gaseous CO_2 to form 1 mol (100 g) of solid CaCO_3 and that the combination of these quantities of reacting substances is attended by the evolution of $43,700 \text{ cal}$, provided that the product, CaCO_3 , is at the same temperature as the reacting substances, which in this case is 18°C .* From the relationship between calories per gram and Chu per pound, it is evident that when 56 lb of CaO combines with 44 lb of CO_2 to form 100 lb of carbonate the heat evolved will be $43,700 \text{ Chu}$ (at 18°C).

The symbols (s) , (l) , and (g) , which are used to indicate whether the substance is respectively in the solid, liquid, or gaseous state, are frequently omitted from the thermochemical equation, but this practice sometimes leads to confusion. For example, the reaction



means that when 1 mol of methane is burnt with oxygen to form carbon dioxide and water and *the water is condensed to liquid* the heat evolution is $212,950 \text{ cal/g mol}$ of methane. On the other hand when *the water is left as vapor* the reaction is



* The pressure is understood to be constant at 1 atm unless otherwise specified.

The difference of 21,040 cal is approximately 10% and is due to the fact that this number of calories is required to vaporize 2 mols of water. Thus, when using heats of reaction one must always make certain that the states of the chemical substances are known to correspond with the values used.

Heat capacities of gases. It is important to remember that, so long as a particular gas behaves as a perfect gas, *i.e.*, conforms quantitatively to the equation $pv = nRT$, its heat capacity, specific heat, energy content, and enthalpy are functions of the temperature only and are independent of pressure and density (or concentration). Thus, the energy that must be abstracted to cool a perfect gas over a given temperature range is independent not only of pressure level but also of the magnitude of pressure drop of the gas in flowing through the equipment in which the cooling is carried out. Deviations from the rule that energy content is independent of pressure can be detected at low pressures in many cases but are often negligible from an engineering standpoint up to fairly high levels of pressure. This rule has great practical utility.

In recent years, highly precise data have been obtained on the heat capacities of various gases normally found in the products of combustion of fuels. Data of somewhat less precision, but nevertheless reliable, are also available on the heat capacities of the lower paraffin and olefin gases. With any of these actual gases, as the pressure is reduced at constant temperature, its observed heat capacity c_p approaches an asymptotic value, c_p° . The heat capacity per mol, or "molal heat capacity," is the product of the molecular weight M and c_p , or Mc_p . Values for the molal heat capacity at zero pressure, Mc_p° , for several gases are plotted in Fig. 1-2.* They are sufficiently close to the values at atmospheric pressure to be used as such in most engineering work.

In engineering calculations, one is usually interested, not in the heat capacity at a particular temperature, but in the quantity of heat absorbed by the gas in the process of being heated, or given up by the gas in the process of being cooled, between two temperature limits. This quantity of heat is the change in the sensible-heat content, or the change in enthalpy, of the gas, and is obtained by integrating the data on heat capacities between two temperature limits. That is, $\Delta h = \int c_p^\circ dt$ between the temperature limits in question, where Δh is the enthalpy change per

* CO_2 , CO , H_2O , H_2 , N_2 , O_2 , CH_4 , main reference: D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Res. NBS* **34**, 143 (1945). H_2O spin correction: C. C. Stephenson and H. O. McMahon, *J. Chem. Phys.* **7**, 614 (1939). OH: H. L. Johnston and D. H. Dawson, *J. Am. Chem. Soc.* **55**, 2744 (1933). NO: H. L. Johnston and A. T. Chapman, *J. Am. Chem. Soc.* **55**, 153 (1933). Hydrocarbons above CH_4 : J. W. Anderson, G. H. Beyer, and K. M. Watson, *Natl. Petroleum News* **36**, R 476 (1944).

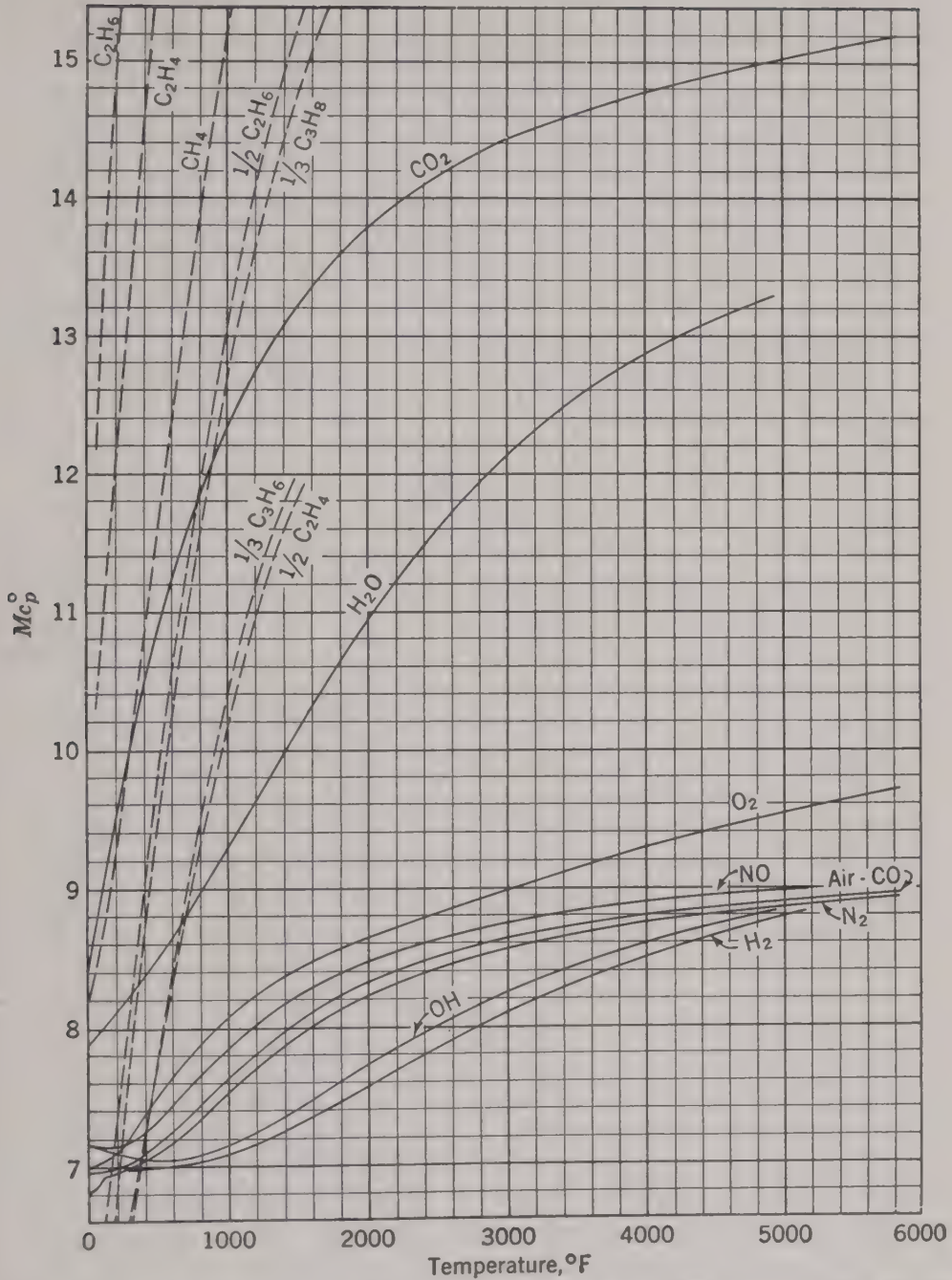


FIG. 1-2. Molal heat capacity of gases at zero pressure Mc_p^0 . The dashed curves are of lower accuracy than the others. (This figure and Fig. 1-3 are supplied through the courtesy of Professor H. C. Hottel of Massachusetts Institute of Technology.)

unit mass. On a molal basis, $M \Delta h = \int M c_p^\circ dt$. If this integration is performed once and for all and the results are summarized in a plot of sensible-heat content against temperature, then heat quantities can be read directly from the plot, without the need for repetitious integrations. On the other hand, for any given size of chart, a plot of heat capacities can be read with much higher precision than a plot of enthalpies, because, over wide ranges of temperature, the percentage change in heat capacity is relatively small. A convenient compromise, which gives the accuracy of a graph of heat capacities and yet avoids the necessity for repeated integrations, is to plot an average heat capacity, defined as sensible-heat content at temperature t , relative to a fixed base temperature t_1 , divided by $t - t_1$. In mathematical terms, the average molal heat capacity is

$$M c_{p,av}^\circ = \frac{\int_{t_1}^t M c_p^\circ dt}{t - t_1}$$

Figure 1-3 is a chart of this type, in which $t_1 = 60^\circ\text{F}$. Values of the sensible-heat content in Btu per pound mol, relative to 60°F , are obtained by multiplying the ordinate $M c_{p,av}^\circ$ by $t - 60^\circ$. If the datum temperature t_1 is not very far from 60°F , there is but a slight difference in the value as read from the chart and the actual value for $M c_{p,av}^\circ$ between t_1 and t , and therefore only a slight error is incurred when multiplying the ordinate by $t - t_1$ to get the sensible-heat content relative to t_1 .

As previously stated, the heat quantity of interest in engineering calculations is usually the change in sensible-heat content between two temperatures. For example, suppose it is desired to know the heat given up by cooling a mol of carbon dioxide gas from 1500°F to 500°F . Its sensible-heat content at 1500°F , relative to 60°F , is

$$11.55(1500 - 60) = 16,630 \text{ Btu/mol}$$

and is $9.92(500 - 60) = 4365 \text{ Btu/mol}$ at 500°F , also relative to 60°F . The heat given up by cooling the gas from 1500°F to 500°F is $16,630 - 4365 = 12,265 \text{ Btu/mol}$. Obviously the average value for $M c_p^\circ$ between these two temperatures is $12,265/1000 = 12.27$. This is quite different from any value read from the chart in this temperature range because it is an average based on 500°F , which is quite different from 60°F on which the chart is based.

From the fact that, in the absence of chemical interaction, the heat effect of isothermal mixing of perfect gases is zero, it follows that the total heat capacity of a mixture is the sum of the heat capacities of its components; *i.e.*, the enthalpy change of the mixture is the sum of the enthalpy changes of the individual components over the same temperature range.

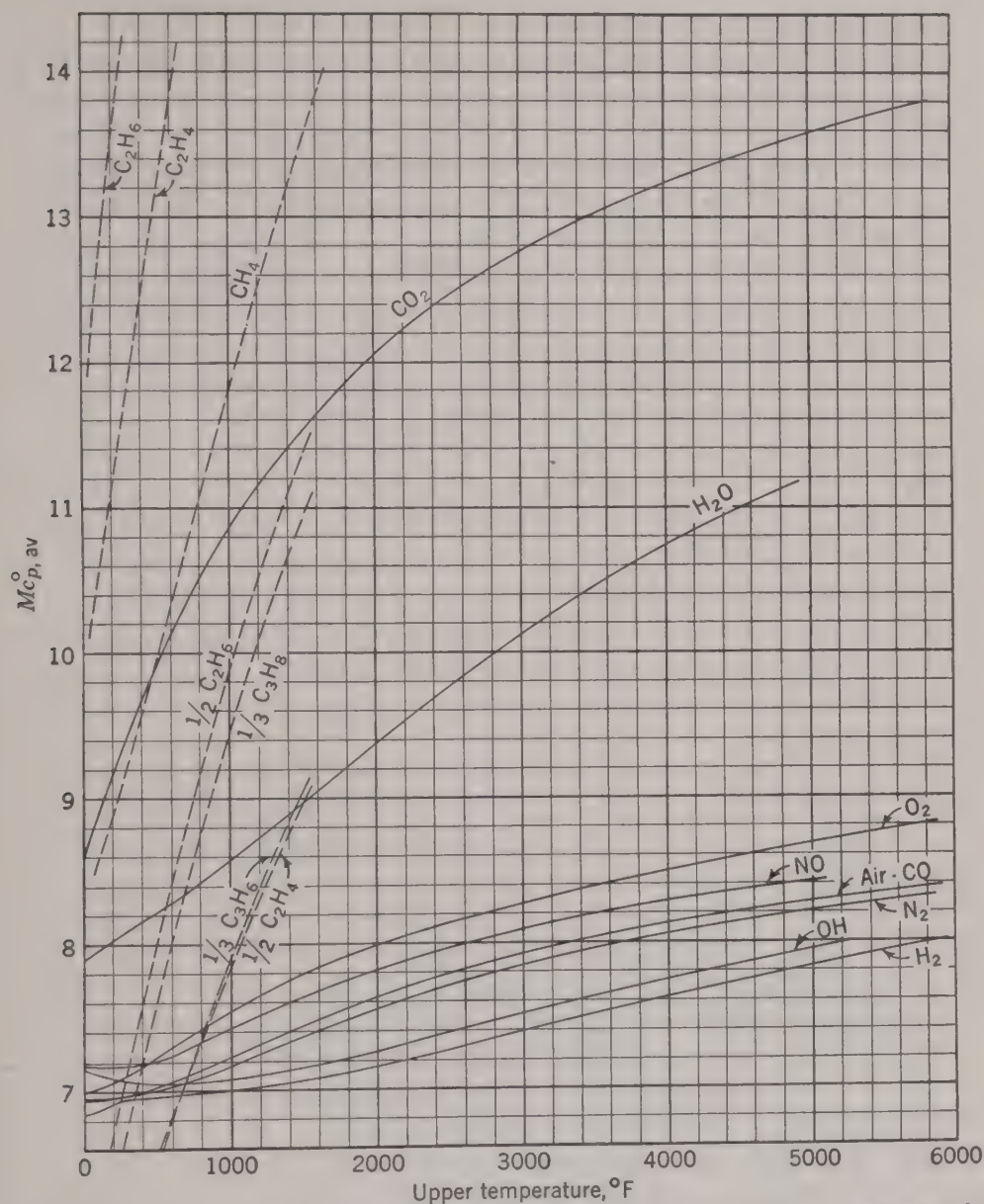


FIG. 1-3. Average molal heat capacity of gases at zero pressure $Mc_{p,av}^{\circ}$, between $60^{\circ}F$ and abscissa temperature. The dashed curves are of lower accuracy than the others.

While this rule breaks down for real gases, the errors introduced by using it are small for moderate deviations from the perfect-gas law.

Thermal properties of liquids. No widely dependable generalizations on liquids have been developed. For water, the steam tables,¹

¹ J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc. New York, 1936. An abridged form of the steam tables is given in Table A-3 in the Appendix.

which are based on direct experimental determinations, should be used. Similar tables or charts have been made for a limited number of other liquids that are commonly used in industry.¹ These tables, when available, are most convenient as they give the heat content or enthalpy directly. When the tables are not available, values of specific heats and heats of vaporization (usually at atmospheric pressure) are to be found in a number of handbooks² and may be used to calculate the heat content of the liquid or vapor. In the absence of any data pertaining to a specific compound, one can estimate the heat of vaporization by using one of several correlations that are available in the literature.

Techniques of computation. Each step in the computation itself, other than mere algebraic transformations, must represent the application of some valid principle or accepted quantitative relationship. The problem is to be able to recognize the principles relevant to the case in hand and to develop the art of applying and combining them to secure the result desired. Some of the most important of these principles are so familiar that one uses them unconsciously, without recognizing them for what they are. Others, such as the gas laws and the laws of combining weights, are usually used as steps in a larger program. The problem of computation is twofold: planning the over-all program, and choosing the principles necessary for its realization.

Ratios and conversion of units. In the main, chemistry is a science whose basic quantitative relationships are simple proportions. An appreciation of this fact greatly simplifies computations, particularly the conversion of units from one system to another. While this fact is emphasized repeatedly in the following chapters, a single illustration will not be out of place at this point. Assume that a sample of gasoline weighing 0.142 g, enclosed in a thin-walled sealed bulb, be introduced up through the mercury of a Torricellian barometer tube inverted in a dish of mercury, the whole jacketed at a temperature of 200°F to ensure complete vaporization of the gasoline. The height of the mercury in the tube above the level in the dish before the introduction of the bulb, corrected for the temperature of the mercury, was 752 mm, and after introducing and breaking the bulb it was 664 mm. The volume of the vapor above the level of the mercury was 310 cc. It is required to deliver, to the intake of an internal-combustion engine, a mixture of this gasoline vaporized in air at a temperature of 100°F, at a concentration such that the partial pressure of the gasoline vapor is 12.5 mm. How many cubic feet of air-vapor mixture must be delivered to the intake per pound of gasoline vaporized?

¹ Perry, *op. cit.*, pp. 249-281; J. B. Maxwell, "Data Book on Hydrocarbons," D. Van Nostrand Company, Inc., New York, 1950.

² Data for a considerable number of compounds are given in the Appendix in the form of alignment charts. For others see Perry, *op. cit.*, or Lange and Forker, *op. cit.*

Proportion offers perhaps the simplest method of solving this problem. The data show that at 200°F and $752 - 664 = 88$ mm absolute pressure, 0.142 g of gasoline vapor occupies the volume of 310 g of water. By proportion, it is, therefore, obvious that, at 200°F and 88 mm pressure, 0.142 lb of gasoline vapor will occupy the volume of 310 lb of water, *i.e.*, $310/62.4 = 4.97$ cu ft. Hence, again by proportion, under the same conditions of temperature and pressure, 1 lb of vapor would occupy $4.97/0.142 = 35.0$ cu ft. At the lower pressure of 12.5 mm,* the volume of vapor is increased in inverse proportion to the pressures to $35.0(88/12.5) = 246.3$ cu ft. Because of the lower temperature, this is reduced in proportion to the absolute temperatures to

$$246.3(560/660) = 209 \text{ cu ft}$$

This is the volume of gasoline-vapor-air mixture which must enter the intake in order to introduce 1 lb of this particular gasoline as vapor if its partial pressure in the mixture is 12.5 mm and its temperature is 100°F.

Note that such a method of attack avoids the necessity of conversion factors from one system to another and, furthermore, makes it possible easily and clearly to visualize the significance of each step of the computation, thereby greatly reducing the chances of errors.

It is important to recognize the principles underlying the successive steps in this calculation. The absolute pressure was computed on the principle of hydrostatics that, in a homogeneous fluid (the mercury), pressure is a function of depth only and pressure difference proportional to difference in depth. That the ratio of the mass of vapor of a given gasoline at fixed temperature and pressure to the mass of water necessary to occupy the same volume as the gasoline vapor is constant, independent of both the magnitude of the masses and the units of mass employed to measure them, is one of those things deemed so obvious that the underlying reason for it is almost never formulated. It may be called the principle of homogeneity—that all the intensive properties of a given material under definite external conditions of temperature and pressure and, in the absence of phase separation, are constant throughout the mass. This includes density, or mass per unit volume, so that fixing total mass fixes total volume and vice versa. The next proportion is a second application of the same principle. The last two steps are of course based on the gas law.

The change in units was made by using the principle of homogeneity in a somewhat more subtle way. Advantage was taken of the fact that, for given conditions, the numerical value of any dimensionless property of a material or system is independent of the units, provided consistent systems of units be employed. The transformation in units might have been made by conversion factors, converting 0.142 g to pounds and 310 cc to cubic feet. Here again one rarely tries to justify the conversion on the basis of principle. After all, 454 g is identical with 1 lb, although not numerically equal to it.

This justification of the use of ratios is given for logical consistency and not because ratios bother the student. Indeed, the man trained in chemistry finds the use of ratios so congenial that he should be encouraged to exploit them to the full.

* Note that the volume of the gasoline depends on its partial pressure alone, and is independent of that of the air mixed with it and occupying the same volume.

Material and energy balances. The application to specific problems of the law of mass conservation is made by what are commonly termed "material balances," *i.e.*, by equating input of material to output for the process under consideration. Material balances can be written for the material as a whole and, where data are available, for the individual chemical elements. Similar balances called "energy balances" that derive their validity from the law of conservation of energy can be set up for the energy effects. Furthermore, each of the equations obtained in writing these balances is independent of the others. Thus, the method of computation most frequently employed in industrial stoichiometry is the equating of input to output, since these equations in some form appear in nearly every problem. The most important factor in the technique of industrial stoichiometry is the mastery of the manipulation of balances of this sort.

Basis of computation. To ensure clarity and accuracy of thinking, it is imperative to visualize exactly the thing under consideration. This thing or quantity about which one is talking is called the "basis" of computation. The "system" in thermodynamics is also the thing about which one is talking, and in energy calculations, "system" and "basis" are often synonymous. However, the use of the two terms often differs. Thus, in a batch operation the system is usually the total mass of matter undergoing change, visualized as isolated materialwise from its surroundings; in material and element balances on the same system, it may often be more convenient to take as the basis a single element or component. Similarly, an element of time may be taken as the basis, although this is usually equivalent to considering a given quantity of matter, which is more satisfactorily indicated or defined in this way. In any event such a "basis" cannot serve as a thermodynamic "system."

In handling a given case it is frequently desirable, if not indeed necessary, to use more than one basis. However, one must never use more than one basis at a time. At various stages in computation it will be necessary to change from one basis to another, but a change in basis should be scrupulously avoided in the middle of any specific computational operation, as one avoids swapping horses in fording a stream. Furthermore, both to eliminate confusion in one's own thinking and to make the computational method clear to anyone checking the results, an unequivocal statement of the basis being employed should appear as a heading for each stage of computation.

Schedule of steps in computation. Long experience has shown the advantage of conformity to the following code, involving a definite sequence of steps to be taken, once the problem and its meaning have been studied carefully:

1. Sketch a diagram or flow sheet. This is the more important the

more involved the process. It is often helpful to indicate all basic data on the sketch itself, and it may be desirable to write on it also the chemical equations and their heat effects.

2. Choose a basis. The first choice may be tentative. One often finds, particularly during the course of solution, that other bases must be adopted and used, at least temporarily.

3. Apply material, element, and component balances.

4. Use energy balances.

5. Apply the known equilibrium relations.

6. Employ the reaction-rate relations.

7. Retrace the foregoing steps and interrelate them as constructively as possible.

As skill develops, one or more of these steps will often be omitted, either as a short cut, or because data for it are lacking or inadequate, or because it does not promise constructive information. However, it is wise to form the habit of checking off each of these steps in order and, if any one is to be omitted, doing this purposefully and not through intellectual default.

Dependability of results. Because material and energy balances are based on laws the validity of which may normally be treated as absolute, the dependability of the results is limited only by the accuracy and completeness of the data available. Thus, stoichiometric methods provide a superlative check on the reliability of industrial data from whatever source, making it possible to detect inconsistencies and errors and avoid unjustifiable conclusions. Obviously, the data on which such computations are based should be collected with care. Samples taken for analysis must truly represent the average compositions of the materials in question. Analyses must be made with accuracy. No sources of loss must be overlooked or neglected. When, however, these precautions have been taken and the data cross-checked by proper methods of computation and comparison, it becomes possible to have justifiable and well-founded confidence in the results and, therefore, in conclusions based upon them.

Material and energy balances are often spoken of as the engineering equivalent of the balance sheet of the accountant. They are far more than this. When the accountant balances his books, it means only that the numerical value of the debit and credit items are such as to check. It does not mean that those items are in fact correct. Thus, there could be an error of 1000 tons in the amount of salt recorded as consumed by a given plant during the month, which would never show up in the accountant's balance sheet. If, however, a material balance for the plant is set up for the month, the discrepancy cannot fail to appear unless it is counterbalanced by other errors that fortuitously cancel it. Moreover, if both sodium and chlorine balances be set up, both will be out of line to an

equivalent amount. Since the balance for each element on which data are available represents a completely independent relationship, equivalent to an independent simultaneous equation in the setting up of the balance, the utility of such balances in detecting and eliminating errors is extraordinarily great. When an operation or process has been analyzed by a series of balances of this sort, the attainment of good balances gives assurance as to the dependability of the data and confidence in conclusions based on the data. This constitutes an extremely important asset for the engineer.

PROBLEMS

1. A paper mill ships to a Texas distributor 12,208 lb of paper. A sample carefully taken at the mill is found by analysis to contain 4.28 % moisture. A sample similarly taken at the destination by the distributor shows 7.88 % moisture. What should be the weight of the shipment as received by him? *Ans.* 12,700 lb.

2. A set of sugar evaporators handles 120 short tons per 24 hr of pure cane sugar, fed to the evaporators as 38% solution and discharged by them as 74% solution. How many pounds of water do these units evaporate per day?

3. A cotton mill dries part of the water-soaked fabric leaving the scouring operation in a drier which delivers the fabric with a residual moisture content of 9% by weight, the fabric in this condition being 6.2 yd/lb. The fabric goes to the drier from the scouring containing 44 % moisture. How many pounds of water are removed by the drying operation per 1000 yd of finished fabric?

4. This mill sizes another part of this same fabric as follows: The scoured fabric containing 44 % moisture is given an initial drying to 30 % moisture. It then passes through an impregnating trough and squeeze rolls in which it imbibes a starch solution, uniformly distributed through it by the rolls. The starch solution in this trough is kept at a uniform level by feeding into it a 12% solution of starch in water to replace that taken up by the fabric. Analysis of the fabric as it leaves the impregnating unit shows that it again contains exactly 44% moisture. It is now given a final drying down to 8% moisture. What is the total water evaporated in the two drying operations per 1000 yd of finished fabric, and what is the weight ratio of dry starch on it to dry fabric?

5. In order to calibrate an orifice, used for metering the flow of dry air in a 2-ft-I.D.-duct at 70°F and 16.2 psia, anhydrous ammonia was bled into the center of the air stream at the rate of 0.251 lb/min. At a distance downstream sufficient to ensure complete mixing of the ammonia and air, the air was analyzed for ammonia content. A small stream of the air was bubbled through 100 ml of 0.0105 N sulfuric acid in an efficient absorption device, and the rate of flow of the sampling stream was measured after absorbing the ammonia by passing the air through a drying tube and collecting the dry air over mercury at 70°F and 1 atm total pressure. The volume of air collected was 0.202 cu ft, and the amount of base (0.00995 N) required for the back titration of the 100 ml of acid was 80.5 ml. Calculate the following:

(a) The rate of flow of air in the duct, expressed as pounds of air per minute.

Ans. 408 lb/min.

(b) The air velocity in feet per second.

Ans. 26 ft/sec.

6. Illuminating gas containing 2.22 vol-% of CO_2 is flowing through a pipe at normal barometric pressure and 75°F. Pure CO_2 is bled into the line from a cylinder at a rate of 3.4 lb/min. A sample of the gas taken from the line at a sufficient distance downstream so that complete mixing has taken place contains 3.71 vol-% of CO_2 . What is the rate of flow of illuminating gas in cubic feet per minute?

7. Moist air is flowing at a steady rate through a pipe line. At section 1 in the line the temperature is 80°F , the total absolute pressure is 753 mm Hg, and the partial pressure of the water vapor in the air is 12 mm Hg. In order to measure the flow rate of the moist air, 15 lb mols/hr of a flue gas at a total absolute pressure of 753 mm Hg and a temperature of 215°F is fed into the line at section 2. The flue gases analyze 18.2% CO_2 , 1.6% O_2 , and 80.2% N_2 on a dry basis; the partial pressure of water vapor in the flue gas is 17 mm Hg abs. At section 3, after complete mixing, the total absolute pressure is 727 mm Hg, the temperature is 92°F , and the analysis is 7.2% CO_2 on a dry basis.

Calculate the pounds per hour of moist air flowing through the pipe line.

8. A plant buys its coal at \$9.20 per ton on a guarantee of a heating value of 13,500 Btu/lb and 7% ash as delivered. It is agreed that handling of the coal costs \$2 per ton and disposal of cinders costs \$3 per ton of cinders. The plant and coal dealer are unable to agree on a sliding scale to allow for deviation of the coal from specification. Assuming the above facts and that the cinders contain no unburned material,

(a) Formulate a price arrangement fair to both parties for determining the price to be paid for a coal with a heating value of Q Btu/lb and $x\%$ ash.

(b) Calculate the price for 15,000-Btu coal with 4% ash.

(c) Calculate the price for 11,000-Btu coal with 12% ash.

9. A tannery extracts mangrove bark containing 4% moisture, 37% tannin, and 23% soluble nontannin material. The residue removed from the extraction tanks contains 62% moisture, 2.8% tannin, and 0.9% soluble nontannin material. What percentage of the tannin in the original bark remains unextracted in the residue?

Ans. 8.0%.

10. A woolen mill extracts the grease from its raw wool by solution in naphtha (volatile organic solvent). The raw wool in a specific batch contained 12% moisture, 30% wool grease, 3% salts (including natural soaps), and 55% fiber. The naphtha extract removed contained 88% naphtha. The extracted wool carried 52% naphtha and 8% moisture. The naphtha was then removed from both the wool and the solution by vaporization and recovered by condensation. The final degreased wool contained 8% moisture and 4% salts and was grease-free. How many pounds of naphtha were removed from the wool by vaporization per 100 lb of final degreased wool?

11. An industrial process for the manufacture of naphthalene-1-5-diamine yields at one stage of the operation a water solution of the base containing 3.01% base by weight. The base is recovered by countercurrent extraction of the aqueous solution with ethyl ether containing 1.25% water by weight. The ether extract is found to contain 15.2% base and 3.67% water on a weight basis. The extracted water layer contains a negligible amount of the base but contains 3.24% ether by weight.

(a) How many pounds of water-free ether were used for the extraction per 1000 lb of base extracted?

(b) What per cent of the ether did the extracted water layer contain?

(c) If the original water solution contained 16.5% by weight of potassium chloride, insoluble in ether, what was the concentration of potassium chloride in the extracted water layer as weight per cent of the solution?

12. In a plant making chlorinated rubber, the vent gases from the chlorinator average in composition 67.1% HCl , 15.5% Cl_2 , and 17.4% CCl_4 (mol per cent). These gases are fed to a Tourill absorber where they are scrubbed with water, the hydrochloric acid formed and the CCl_4 condensed being separated and pumped to separate tanks. The exit gases from the Tourills average in composition 29.5% HCl , 42.6% Cl_2 , and 27.9% CCl_4 (mol per cent). The tower is producing 31.7% by weight hydrochloric acid and the water rate at the top of the tower is 100 lb/hr. The CCl_4 contains 8.95% by weight free chlorine. A negligible amount of free chlorine is dissolved in the hydrochloric acid. Calculate the following:

- (a) The pounds per hour of hydrochloric acid produced.
- (b) The feed rate of gas to the Tourills in pound mols per hour.
- (c) The per cent recovery of HCl.
- (d) The per cent recovery of CCl_4 .

13. A pan contains 6420 lb of an aqueous solution at 104°C , 29.6% of which is anhydrous sodium sulfate. The whole is cooled without evaporation to 20°C , at which temperature crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ separate. The remaining solution (mother liquor) is found to contain 16.1% anhydrous Na_2SO_4 . What is the weight of this mother liquor?

Ans. 3340 lb.

14. Sodium sulfide is produced by reduction with coal screenings of salt cake (Na_2SO_4) obtained from Mannheim furnaces. The reduction takes place in an oil-fired, horizontal, rotary furnace and the "black ash" produced, containing the sodium sulfide, is leached with hot water. The solution leaving the leaching pans is at 90°C and contains 27.2% Na_2S . This solution is pumped to crystallizing pans, where crystals of the composition $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ separate out. The mother liquor leaving the crystallizing pans is at 18°C , at which temperature the solution saturated with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ contains 13.3% Na_2S . In connection with a survey of the operation of this plant, it has become necessary to calculate the maximum yield of crystals per 1000 lb of solution fed to the pans under the following assumed conditions of operation:

- (a) No evaporation of water during crystallization.
- (b) Water evaporation during crystallization equal to 10% by weight of the water of hydration in the separated crystals.

15. The following approximate figures are available on the operation of a magnesium plant. The raw material is a brine containing MgCl_2 and CaCl_2 in the weight ratio of 1:3. This brine is fed to evaporators. As evaporation proceeds, crystals of tachydrate ($2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$) separate out. The residual liquor leaving the evaporators, containing MgCl_2 and CaCl_2 in the weight ratio of 1:10, is treated with lime to precipitate $\text{Mg}(\text{OH})_2$, which is then treated with H_2SO_4 to form Epsom salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). The tachydrate crystals from the evaporators are dissolved in hot water and cooled in crystallizers, separating out $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which is put through a dehydrating operation and then used as charge for electrolytic cells to produce Cl_2 and metallic Mg. The mother liquor from the crystallizers, which has a weight ratio of MgCl_2 to CaCl_2 of 1:1, is sent back to the evaporators.

- (a) Of the Mg present in the raw brine, what per cent goes to the cells?
- (b) Of the Mg entering the crystallizers, what per cent leaves the crystallizers in the mother liquor?

16. The stable form of sodium sulfate in equilibrium with aqueous solutions at 10°C is Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Its saturated solution at this temperature contains 8.4 wt-% of anhydrous Na_2SO_4 . At 100°C the stable form is Na_2SO_4 and its solubility similarly expressed is 29.6 wt-%.

- (a) If a 29-wt-% solution of anhydrous salt be cooled from 100°C to 10°C and 12% of its initial water be lost by evaporation during the process, what fraction of the total sulfate content would be expected to crystallize out?

(b) After the above crystallization, the mother liquor is drained from the crop. However, because of adhering mother liquor, 3.1% by weight of the crop is water of solution, *i.e.*, in excess of water required to make $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ from the total amount of Na_2SO_4 present in the crystals and adhering liquor. How much water is required for the initial solution of the original salt, per 1000 lb of Glauber's salt obtained as the final product after drying off the water of solution?

Chapter 2

GASEOUS AND LIQUID FUELS

Gaseous fuels. Substantially all gaseous fuels are mixtures, the analysis of which is designed to identify each chemical component and determine its amount. Occasionally identification is incomplete. Thus, olefins, usually present in small amounts, are often lumped together.¹ Natural gas contains saturated paraffin hydrocarbons, predominantly methane, together with other gases (nitrogen, carbon dioxide, etc.), usually small in amount. The principal constituents in the manufactured, so-called secondary, gaseous fuels² are hydrogen, carbon monoxide, and hydrocarbons, often accompanied, however, by considerable amounts of nitrogen, carbon dioxide, etc. The analyses are almost always volumetric, conducted at atmospheric pressure, with the results reported as volume per cent, identical with mol per cent except for minor deviations from the gas laws. Wherever a gas analysis is reported otherwise it is imperative to state the fact.

The nitrogen in these gases usually comes largely or exclusively from air, which is introduced in the course of their manufacture. It is almost always determined as chemically inert residual gas and includes the noble gases present in the air.

¹ In gases formed at high temperature levels, any olefin present is predominantly ethylene and is ordinarily reported as such. In mixtures in which, because of their origin, it is known that higher olefins are likely to exist, the total olefins are not infrequently reported as a single compound, *e.g.*, propylene. This is a rough method of averaging their molecular weights.

² As will develop later, the most essential thing about the composition of any organic fuel, gases included, is its content of carbon and available hydrogen. In gas analysis these elements when present in the form of hydrogen, saturated hydrocarbons, and even CO are in fact usually determined by the so-called combustion technique. It is surprising that the chemical engineer has not developed the practice of submitting the total original fuel gas directly to this technique, *i.e.*, burning it completely in a single initial operation, because this would furnish exactly the information which the combustion engineer needs to know, namely, the carbon content of the fuel and the total oxygen required to burn it. Only rarely is he interested in the chemical constituents actually present in the fuel he burns.

Liquid fuels. The liquid fuels commonly met consist largely of carbon and hydrogen, with little or no oxygen and only traces of ash. They frequently contain small amounts of sulfur and occasionally some nitrogen.

GAS ANALYSIS

Before useful combustion calculations on the total, over-all performance of operating combustion devices can be made, not only must the ultimate composition of the fuel be known, or at least estimated, but also an accurate analysis of the gaseous products of combustion must be made. In the usual case such an analysis is secured by the standard Orsat technique or one of its modifications.¹

Effect of water vapor. An important point in gas analytical procedures of the Orsat type is the fact that the results of analyses conducted in the presence of liquid water, and therefore under saturated conditions, are on a dry, *i.e.*, water-free, basis. Even when mercury is used as the confining liquid in the gas-measuring burette, one maintains a drop of water on top of the mercury column in order that the confined gas will always be saturated.

Since an analysis is always determined at a constant temperature, the vapor pressure of water will remain constant throughout the procedure, *i.e.*, about 18 mm Hg at normal room temperature. Similarly, because the gas volumes are measured at atmospheric pressure, the partial pressure of the water vapor present in the gas mixture at any time will always be the same fraction of the total pressure, *i.e.*, 18/760 atm (assuming normal barometer).

If, for example, the total volume is halved by absorption of one component, half the water vapor originally present must necessarily condense in order to maintain constant its partial pressure. In other words, throughout an analysis the total pressure of the gases other than water vapor is always equal to atmospheric pressure minus the vapor pressure of water, *e.g.*, $760 - 18 = 742$ mm. The net effect, therefore, is that of an analysis carried out on a dry gas at a constant pressure of 742 mm.

Errors in the determination of CO_2 . Aside from the question of securing a representative gas sample, the accuracy of the analysis and, therefore, the precision of the subsequent calculations are seriously affected by the type of confining liquid employed in the gas-measuring burette of the Orsat apparatus. When mercury is used for this purpose, the results obtained are generally reliable if sufficient care is taken in the manual operation of the analysis. Frequently, however, water is substituted for mercury because of convenience and the cost of mercury.

¹ These use selective liquid absorbents in series and measure decrease in volume after each absorption. Sometimes chemical transformations of components in the sample are effected between successive absorptions.

Because of the appreciable solubility of CO_2 in water, analyses secured under this condition may be of questionable value in combustion calculations.

Consider, for example, the analysis over water of a gas mixture containing 10% CO_2 and 90% N_2 . Assume that in drawing the gas sample into the burette, 101 ml is in fact introduced but that 1 ml of the CO_2 dissolves, leaving 100 ml as the apparent volume of the gas sample. As the gas is passed through caustic to remove the CO_2 , the total volume will decrease to 90.9 ml, that of the nitrogen. However, if the sample is allowed to stand for a short time in the measuring burette, the gas volume will again increase slightly as the dissolved CO_2 comes out of solution because of the reduced CO_2 partial pressure in the gaseous phase. A constant value of 90.9 ml will not be obtained, therefore, until all the CO_2 has been removed from its solution in the confining liquid. Since the total apparent decrease in volume ultimately realized is 9.1 ml, the per cent CO_2 as reported would be 9.1%, or an error of $100(10 - 9.1)/10 = 9\%$ in the amount of CO_2 actually present. By using an acidified concentrated salt solution as the confining liquid, the error can be reduced but not eliminated.

The practical effect of this error will be illustrated in a subsequent example and a method of approximation for use under these circumstances presented. For the moment, however, it is obvious that, unless mercury is used as the confining liquid, the reported analysis for CO_2 is subject to question.

Determination of components present in small amounts. Conventional methods of gas analysis using liquid absorbents are gravely defective when employed for components present in very small amounts. The difficulty due to determination of a small difference between two large gas volumes (the shrinkage on absorption) is obvious. However, the most serious problem is caused by the solubility of the remaining components of the gas sample in the absorbing liquid being employed for the specific component under determination. Thus, there are gases that, from the very nature of the processes producing them, can contain no significant quantity of elementary oxygen. Nevertheless, the analyses of such gases frequently indicate small quantities of oxygen. This may be due to contamination of the original gas with air in the process of sampling or upon its introduction into the analytical apparatus. On the other hand, similar questionable results may be obtained even after great care has been taken to prevent air contamination. This difficulty is usually due to solution of a small fraction of the residual gases of the sample in the pyrogallate or other oxygen-absorbing solution used in the analysis. Thus, in a gas from which the CO_2 has been absorbed, containing CO , H_2 , and various hydrocarbons and residual nitrogen, a small fraction of these gases will dissolve in the pyrogallate solution, unless it

has already been saturated with them. The shrinkage in volume following exposure of the gas sample to pyrogallate will be reported as oxygen. Theoretically, the pyrogallate could be saturated with these residual gases before use on the sample in question, but the technique of doing so may be difficult. The error is obviously largest when fresh, relatively gas-free solutions are employed. Where solutions are used for successive analyses of gas samples, all of which are of nearly the same composition, each absorbent solution approaches equilibrium with the gas mixture left after absorption of the component it is designed to remove. Thus the error gets progressively less but reappears when the exhausted solution is renewed. Where the composition of the gas samples being analyzed changes, the error persists and may even become negative, gas coming out of solution and increasing the volume of the sample.

What to do in situations of this sort demands judgment. If an exact determination of a specific component present in small amount is necessary, one should resort to suitable analytical techniques and not depend upon the usual liquid absorption methods. If the circumstances justify the assumption that oxygen, for example, is due to air leak, it, together with its corresponding nitrogen, can in the process of computation be eliminated from the analytical result. If the indicated presence of a trace of some component is believed to be due wholly or in part to solution of the rest of the gas mixture in the absorbing liquid, it may be difficult to decide exactly how to proceed. Sometimes one is justified in assuming that the shrinkage in volume is due to absorption of the remaining gases in the same proportion as that in which they exist in the original mixture. This would be the case if these gases have substantially identical solubilities and the liquid absorbent contains no dissolved gas, or if there are other grounds for assuming identical relative absorption rates. The best solution to the problem is a careful analytical technique, always critically evaluated. However, the engineer is frequently faced with data the constructive interpretation of which demands suitable approximations based on legitimate assumptions, the nature of which must be determined for each specific case.

CALCULATIONS BASED ON FUEL ANALYSIS

By the use of element balances, one can calculate from the fuel analysis alone both the amount of air required for a theoretical combustion of the fuel, in which all combustible elements are completely oxidized, and the actual combustion-gas composition for any per cent excess air and degree of completeness of combustion. The term "excess air" is usually defined as the amount of air used above that theoretically needed for complete combustion, *i.e.*, to burn carbon and hydrogen, or compounds of the two, to carbon dioxide and water. The per cent excess air is the

ratio of the excess to the theoretical amount, multiplied by 100. It is conveniently interpreted in terms of oxygen instead of air.

In the discussion immediately following, it will be assumed, for the sake of simplicity, that both air and fuel are dry. The technique of allowing for the presence of water in fuel and air will be considered at a later point.

Combustion of carbon. If one were to burn pure carbon (charcoal or coke, free of hydrogen) with the theoretical amount of air, CO_2 would replace the O_2 in the air, mol for mol, and the analysis of the combustion gases would necessarily be 21.0% CO_2 and 79.0% N_2 .* If, on the other hand, 50% excess air were used, only two-thirds of the O_2 in the air would be replaced by CO_2 , and the analysis of the flue gas under such conditions would be 14.0% CO_2 , 7.0% O_2 , and 79.0% N_2 .

The formation of CO , due to incomplete combustion, *i.e.*, oxidation of carbon, involves another step in calculation, because the reaction, $2\text{C} + \text{O}_2 = 2\text{CO}$, shows that 2 mols of CO are obtained for each mol of O_2 . Suppose that hydrogen-free coke is burnt under such conditions that 75% of the carbon burns to the monoxide, the rest to dioxide, and no free O_2 remains in the combustion products. This means that on burning 100 atoms of carbon there will be formed 75 mols of CO and 25 mols of CO_2 ; the O_2 required, therefore, will be 37.5 mols for the former oxide and 25 for the latter, making a total O_2 consumption of 62.5 mols. To obtain this oxygen from air requires the introduction of nitrogen in the amount of 62.5 (79/21) = 235 mols. All the components of the combustion gas are now available, and they may be arranged as in the following table to obtain the percentage composition.

Basis: 100 atoms of C in fuel.

Component of combustion gas	Mols	Fraction	Per cent
CO	75	75/335	22.4
CO_2	25	25/335	7.45
N_2	235	235/335	70.15
Total combustion gases.....	335	100.0

Another basis that may be used to compute the same result is 100 mols of air. On this basis, 79 mols of N_2 must appear in the combustion gases. Of the 21 mols of O_2 in the air, the amount going to CO is in the proportion of 37.5:62.5, or 12.6 mols, forming 25.2 mols of CO . The rest of the oxygen, 8.4 mols, yields the same number of mols of CO_2 . The following table summarizes these calculations.

* Throughout this book, air is assumed to contain 21.0% O_2 by volume. This is perhaps high by a few hundredths of a per cent. The nitrogen includes the noble gases.

Basis: 100 mols of air.

Component	Mols	Fraction	Per cent
N ₂	79	79.0/112.6	70.15
CO.....	25.2	25.2/112.6	22.4
CO ₂	8.4	8.4/112.6	7.45
Total combustion gases.....	112.6	100.0

Another way of attacking the same problem is to use an algebraic approach. Take as a basis 100 atoms of carbon. A sketch such as Fig. 2-1 will aid in visualizing the problem. Note that the figures under "Air" are not quantities but compositions. Let x = the mols of air

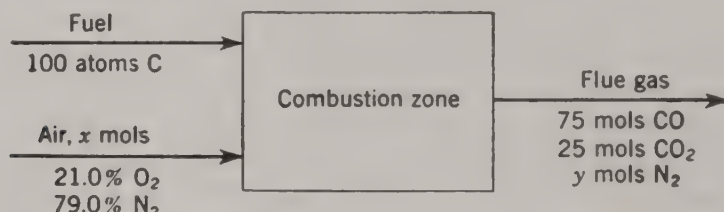


FIG. 2-1. Incomplete combustion of carbon.

and y = the mols of N₂ in the flue gas. Since there are two unknowns, solution of the problem requires two principles or relationships that can be expressed as equations. The principle of a carbon balance has already been used in the construction of the sketch itself, but oxygen and nitrogen balances have not. By an oxygen balance, $0.21x = 25 + 37.5 = 62.5$. By a nitrogen balance, $0.79x = y$. Hence $y = 0.79(62.5/0.21) = 235$. The results are the same as those first tabulated above.

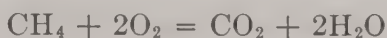
Basis: 100 atoms of carbon.

Component	Mols	Per cent
N ₂	235	70.15
CO.....	75	22.4
CO ₂	25	7.45
Total combustion gases.....	335	100.0

The simplicity of the above equation for y as well as the identity of results suggest the first method of solution, which is perhaps best described as the method of ratios. The sketch of the process shows that the total O₂ in the flue gas amounts to 62.5 mols; all the O₂ and N₂ in the flue gas come from a single source, the air; the ratio of N₂/O₂ in the air is 79/21; therefore, N₂ in the flue gas must be equal to $62.5(79/21)$, or 235 mols.

Combustion of hydrogen. The presence of hydrogen in the fuel involves still another point. Pure hydrogen when completely burnt with theoretical air will, in effect, remove the oxygen from the air as water. The combustion gases will be water vapor and nitrogen, provided they are at some temperature above the condensation point of the water contained in them. The gas analysis, however, does not show the presence of water, as it is condensed before and during the analysis, the resulting figures being on a dry basis. The analysis is, therefore, 100% N₂. With excess air, the corresponding oxygen will appear in the gas, with a decrease in the percentage of nitrogen.

Combustion of hydrocarbons. Consider a mol of methane burning with 90% excess air. The equation for complete combustion may be written



Thus there will be obtained 1 mol CO₂ and 2 mols H₂O from complete combustion of 1 mol CH₄. The oxygen required is 2 mols, and if 90% excess is used, this means an additional 1.8 mols, or a total of 3.8 mols of oxygen. The nitrogen which comes into the furnace along with the oxygen is 3.8 (79/21) = 14.3 mols, giving a total of 19.1 mols of wet gas, but only 17.1 mols of water-free gas. In the latter, the CO₂ will be (1/17.1)100, or 5.85%; the O₂, (1.8/17.1)100, or 10.5%; and the N₂, (14.3/17.1)100, or 83.65%.

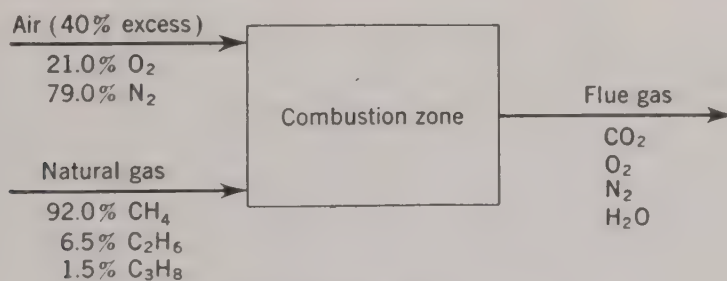
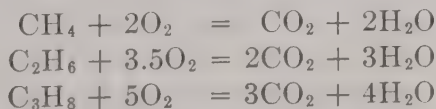


FIG. 2-2. Combustion of natural gas.

The behavior of hydrocarbon mixtures may be illustrated by the combustion of a natural gas, containing 92.0% CH₄, 6.5% C₂H₆, and 1.5% C₃H₈ with 40% excess air. A diagrammatic sketch of the operation is seen in Fig. 2-2. The equations for combustion are



As a basis for computation, choose 100 mols of fuel gas. Calculations of theoretical O₂ and combustion products are perhaps most conveniently

carried out by making up a table with the headings shown below and filling in the various columns.

Basis: 100 mols of fuel gas.

Component	Mols	Theoretical O ₂	CO ₂ formed	H ₂ O formed
CH ₄	92.0	184.0	92.0	184.0
C ₂ H ₆	6.5	22.8	13.0	19.5
C ₃ H ₈	1.5	7.5	4.5	6.0
Total.....	100.0	214.3	109.5	209.5

Excess O₂ in the flue gases is 0.40(214.3), or 85.7 mols. Total O₂ is 214.3 + 85.7 = 300.0 mols and the corresponding N₂ from the air is 300(79/21) = 1130 mols. This gives all components in the dry flue gas.

Basis: 100 mols of fuel gas.

Component	Mols	Per cent
CO ₂	109.5	8.3
O ₂	85.7	6.5
N ₂	1130.0	85.2
Total.....	1325.2	100.0

In the case of liquid hydrocarbon fuels, the analysis in terms of individual chemical compounds is rarely known. It is usually most convenient to take as a basis for computation a given weight of the fuel, *e.g.*, 100 lb. For ease in the determination of stoichiometric relationships, it is advisable to compute and employ the pound atoms of the individual elements in the basic 100 lb. In the case of hydrogen, it is frequently more convenient to express the amount present as mols of H₂, since each of these is equivalent in combustion to one atom of oxygen. Computation of the analysis of the products of combustion of a fuel oil containing 88.2% C and 11.8% H, when burnt with 20% excess air according to the process of Fig. 2-3, under conditions such that all the hydrogen is converted to water and 95% of the C to CO₂ and the rest to CO, will serve as an illustration.

Consider 100 lb of the oil as a basis and find the number of atoms or mols of each constituent.

$$\begin{aligned} 88.2/12 &= 7.35 \text{ atoms C} \\ 11.8/2.016 &= 5.85 \text{ mols H}_2 \end{aligned}$$

CO₂ in the flue gas is 7.35(0.95), or 6.98 mols; CO is 7.35(0.05), or 0.37

mol; and H_2O is 5.85 mols. Theoretical O_2 is $7.35 + (5.85/2)$, or 10.28 mols. The excess O_2 in the entering air is $10.28(0.20)$, or 2.06 mols. However, the free O_2 in the flue gas is 2.06 mols plus the amount of O_2 unused by the carbon because of its burning only to CO . This latter is $0.37/2 = 0.19$ mol, giving a total of 2.25 mols of free O_2 in the flue gas.

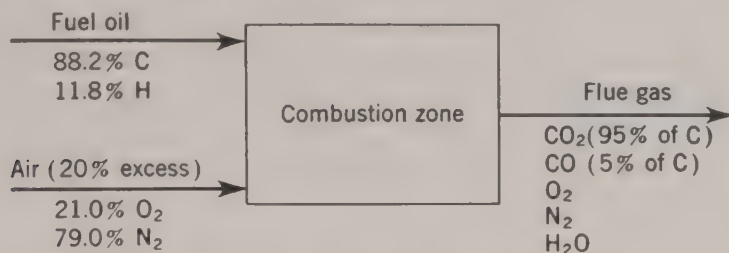


FIG. 2-3. Combustion of fuel oil.

N_2 is $(10.28 + 2.06)(79/21) = 46.5$ mols. The results may now be arranged as previously, omitting the water vapor formed.

Basis: 100 lb of fuel oil.

Component	Mols	Per cent
CO_2	6.98	12.4
CO	0.37	0.7
O_2	2.25	4.0
N_2	46.5	82.9
Total.....	56.1	100.0

Correction for nitrogen in the fuel. When the complete analysis of a fuel is available, little complication is introduced by the presence of significant quantities of nitrogen. In making calculations on the amount of nitrogen in flue gas, one merely adds the nitrogen from the fuel to that from the air. For illustration, consider the combustion of a mixture of 1 mol of methane and 1 mol of nitrogen burning with 90% excess air. As shown in a previous example (page 29), there will be obtained 1 mol of CO_2 , 2 mols of H_2O , 1.8 mols of O_2 , and 14.3 mols of nitrogen from the air. To the latter must be added the nitrogen in the fuel, making a total of 15.3 mols of nitrogen in the flue gas and 18.1 mols of water-free gas. On a dry basis, the CO_2 will be $1/18.1$, or 5.53%, the O_2 , $1.8/18.1$, or 9.95%, and the N_2 , $15.3/18.1$, or 84.52%.

Correction for oxygen in the fuel. Oxygen is most frequently met in gaseous fuels in the form of CO , CO_2 , or free O_2 and is often present in liquid fuels in various types of oxygenated organic compounds. CO is commonly encountered as a major constituent in the so-called secondary

fuels. A theoretical water gas, *i.e.*, an equimolal mixture of CO and H₂, burning with 30% excess air but with only 90% of the CO being converted to CO₂ and 95% of the H₂ to H₂O, would be an example. The 0.5 mol of CO and of H₂ contained in a mol of this water gas would each require 0.25 mol of O₂, a total of 0.5 mol, for theoretical combustion. Using 30% excess, the O₂ employed would be $1.3(0.5) = 0.65$ mol. The oxygen present in the combustion products may be considered as made up of two kinds: (1), the 0.15 mol used in excess of that required for theoretically perfect combustion, and (2) 10% of the 0.25 mol theoretically required by the CO plus 5% of the 0.25 mol needed for the H₂, but not used in the combustion. It is now easy to find the amounts of the various gases and the percentage composition.

Basis: 1 mol of water gas.

	Mols	Fraction of total	Per cent
90% of 0.5 mol CO.....	0.45 CO ₂	0.45/3.16	14.2 CO ₂
10% of 0.5 mol CO.....	0.05 CO	0.05/3.16	1.6 CO
5% of 0.5 mol H ₂	0.025 H ₂	0.025/3.16	0.8 H ₂
0.15 + 0.10 (0.25) + 0.05(0.25)...	0.188 O ₂	0.188/3.16	5.9 O ₂
0.65(79/21).....	2.445 N ₂	2.445/3.16	77.5 N ₂
Total water-free gas.....	3.16	100.0
95% of 0.5 mol H ₂ = H ₂ O.....	0.475		
Total gas; including water vapor	3.64		

Oxygen in a fuel gas in the form of CO₂ is treated in somewhat the same way as nitrogen in the fuel, *i.e.*, CO₂ in the fuel is simply added to the CO₂ from burning of combustibles to give the total amount of CO₂ in the flue gases. If a fuel gas contains free O₂, the usual practice in computing the theoretical air requirement is to sum the theoretical requirements of O₂ for complete combustion of each of the combustible elements in the fuel and then subtract the free O₂ in the fuel itself.

While certain liquid fuels contain appreciable quantities of oxygen, it is practically always true that hydrogen is present in excess of that stoichiometrically equivalent to the oxygen. For purposes of combustion calculations, it is convenient to assume arbitrarily that all the oxygen present is in the form of water of chemical combination. The excess of hydrogen over that in this combined water is then termed *available* or *net* hydrogen, *i.e.*, hydrogen requiring oxygen from a source outside the fuel for its combustion. The use of these concepts is illustrated by the combustion of a lignite pitch, containing 80% C, 10.8% H, 8.2% O, 1.0% N, and a trace of sulfur. If this fuel is completely burned with 60% excess air, the products of combustion are determined as follows:

Basis: 100 lb of pitch.

Component	Pounds	Atoms or mols*	Theoret- ical O ₂	Products of combustion			
				CO ₂	H ₂ O	O ₂	N ₂
C.....	80.0	6.66	6.66	6.66			
H ₂	10.8	5.36					
O.....	8.2	0.51					
N ₂	1.0	0.04	0.04
Total.....	100.0						
Net H ₂ , 5.36 - 0.51.....		4.85	2.43	4.85		
Combined H ₂ O.....		0.51	0.51		
Total.....			9.09				
N ₂ from air, 9.09(1.60)(79/21).....					54.7
Excess O ₂ , 9.09(0.60).....				5.45	
Total.....				6.66	5.36	5.45	54.74

* The symbol in the component column determines whether one is using mols or atoms.

Although it was noted in the preceding paragraph that most fuels contain hydrogen in excess of that equivalent to the oxygen content, it must not be assumed that this is invariably true. Thus, in burning pure cellulose, the empirical formula of which is $C_6H_{10}O_5$, the compound itself contains oxygen equivalent to the hydrogen, and the oxygen that must be supplied from the air is that equivalent to the carbon alone. If it is granted that 50% excess air is supplied in the combustion process and combustion is complete, the net effect is the same as in burning pure carbon. Since the water formed by the reactions will not show up in the Orsat analysis, the analysis of the combustion gases will be 14% CO₂, 7% O₂, and 79% N₂.

Correction for sulfur in the fuel. Under normal oxidizing conditions of furnace combustion, sulfur is converted chiefly to SO₂. In most cases a small amount of SO₃ is also formed,¹ but in the majority of fuels sulfur is only a small fraction of the total combustible material, and little error is introduced into the over-all results if it is assumed that all sulfur in the flue gases is present as the dioxide.

Complications exist in the analysis of flue gases containing significant percentages of SO₂. One cause of difficulty, sometimes overlooked, is the high solubility of SO₂ in water, which makes it impractical to analyze for SO₂ in an Orsat apparatus in which water or a salt solution is used as the confining liquid in the measuring burette. Another handicap is the fact

¹ One must take account of this fact in the combustion of sulfur and sulfide ores (see Chap. 6).

that the amount of SO_2 present in fuel combustion gases is usually too small to be determined dependably by selective absorption in apparatus of the Orsat type. One common practice is to conduct the analysis over mercury, absorbing SO_2 and CO_2 simultaneously. The sum of the two compounds is then ordinarily reported as CO_2 . When this technique is used, the amount of water placed on top of the mercury to saturate the gas sample in the measuring burette should be as small as practicable, in order to minimize the amount of SO_2 it can absorb. Another technique is to draw the gas sample into the Orsat apparatus through a selective absorbent for SO_2 , such as PbO_2 , in which case the gas absorbed in alkali is CO_2 alone.

The difference between the two methods of analysis is illustrated (see Fig. 2-4) by the combustion of a fuel oil containing 87.2% C, 8.6% H, and 4.2% S with 30% excess air, under conditions such that 5% of the carbon in the fuel is burnt to CO and the rest to CO_2 , while the hydrogen is completely oxidized.

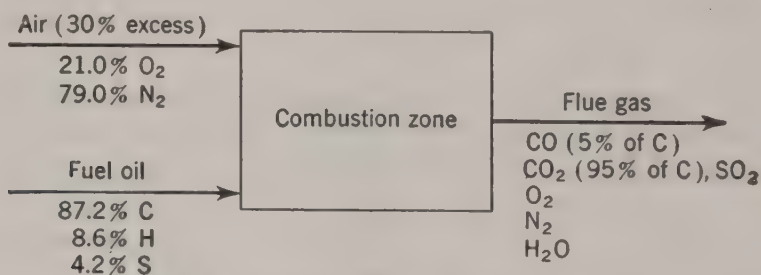


FIG. 2-4. Combustion of a high-sulfur fuel oil.

Let the basis of calculation be 100 lb of oil. Find the atoms or mols of each element therein, and determine the theoretical O_2 and products of combustion.

Basis: 100 lb of oil.

Element	Pounds	Atoms or mols	Theoretical O_2
C.....	87.2	7.26	7.26
H ₂	8.6	4.27	2.14
S.....	4.2	0.13	0.13
Total.....	100.0	9.53

In the products of combustion, SO_2 is 0.13 mol; CO_2 is 7.26(0.95), or 6.90 mols; CO is 7.26(0.05), or 0.36 mol; O_2 is 9.53(0.30) + (0.36/2) = 3.04 mols; N_2 is 9.53(1.30)(79/21) = 46.5 mols; and H_2O is 4.27 mols. On a water-free basis, the flue gas is 56.93 mols, whereas on a water-free and

SO₂-free basis, it is 56.80 mols. Accordingly, if SO₂ is removed by PbO₂, the percentage of CO₂ reported by Orsat analysis should be $6.90(100/56.80) = 12.15\%$. Were there no removal of SO₂ prior to analysis, the reported percentage of CO₂ should be

$$(6.90 + 0.13)(100/56.93) = 12.35\%$$

The small difference in the amounts of gas absorbed by alkali in the course of the analysis, despite the high sulfur content of the fuel, should be noted. In view of the recognized limitations of gas analytical techniques, it is clear that one must be careful in the interpretation of the results in the case of fuels containing sulfur.

CALCULATIONS BASED ON FLUE-GAS ANALYSIS

Net-hydrogen/carbon ratio in the fuel and per cent excess air.

If a fuel containing negligible nitrogen and sulfur is fired under conditions such that there are no losses of combustible matter in soot or refuse, the flue-gas analysis alone is sufficient to enable calculation of the net hydrogen-carbon ratio in the fuel and the per cent excess air employed in combustion. Mathematically, the reasoning is equivalent to setting up a nitrogen balance, equating the nitrogen in the flue gas to that in the air employed, and using this equation to solve for the total oxygen that went into the flue gas from the air. This is followed by an oxygen balance, which is solved for the otherwise unknown amount of oxygen going to burn hydrogen to form water. The method is illustrated by the following examples.

Illustration 1. The combustion gases from a certain furnace using a nitrogen-free fuel are analyzed carefully by the Orsat technique and are found to contain 16% CO₂, 5% O₂, and the rest inert gases. What do these figures mean?

Take as a basis for computation 100 mols of this gas as analyzed. As appears in the following table, the analysis shows the presence of 21 mols of O₂. By difference, 79 mols of N₂ is found in the gases. Since there was no N₂ in the fuel, all this N₂ must have entered the furnace with the air for combustion. The oxygen associated with this N₂ is

$$79(21/79) = 21 \text{ mols}$$

Basis: 100 mols of gas as analyzed.

Gas	Mols	Mols O ₂	Atoms C
CO ₂	16	16	16
O ₂	5	5	

Since all the oxygen consumed appears in the gas analysis, the fuel contains no net hydrogen. If there were any hydrogen in the fuel, there was also sufficient oxygen to combine with it, *i.e.*, the combustible matter of the fuel was $C(H_2O)_n$. The fuel could have been coke ($n = 0$) or, *e.g.*, a carbohydrate. The per cent excess air for the combustion is

$$(5/16)100 = 31.3\%$$

Illustration 2. The flue gas from a certain furnace burning a fuel of negligible nitrogen content is found by analysis to contain 12% CO_2 , 7.5% O_2 , and 80.5% N_2 . What conclusions can be drawn from these figures?

Take as a basis for computation 100 mols of this gas as analyzed. As appears from the following table, the analysis shows the presence of 19.5 mols of O_2 . The nitrogen came, however, from the air used for combustion and hence brought with it 21.4 mols of O_2 . Oxygen has, therefore, disappeared from the gas as analyzed, and this disappearance of 1.9 mols of O_2 must be caused by and correspond to the combustion of the net hydrogen in the fuel. The hydrogen burnt is, therefore, 3.8 mols. The water formed by this combustion, together with any other which may have been present, was condensed before and during the analysis.

Basis: 100 mols of dry gas.

Component	Mols	Mols O_2
CO_2	12.0	12.0
O_2	7.5	7.5
N_2	80.5	
Total.....	100.0	19.5 O_2 accounted for
80.5(21/79).....		21.4 O_2 from air
O_2 unaccounted for by analysis.....		1.9 O_2 disappearance

H_2 burnt to H_2O , $2(1.9) = 3.8 H_2O$ from combustion

This 100 mols of dry gas contains 12 atoms, or 144 lb, of carbon, which came from the fuel and hence represents the carbon burnt, though it does not include any carbon left as unburnt combustible mixed with the ash or elsewhere. This carbon burnt was accompanied by 3.8 mols, or 7.65 lb, of net hydrogen in the fuel. Hence, for each pound of carbon burnt, the dry flue gas was $100/144 = 0.695$ mol, or 249.4 cu ft under standard conditions. Furthermore, except for water in the air or fuel used, the total flue gas was $103.8/144 = 0.722$ mol, or, at standard conditions, 259 cu ft per pound of carbon burnt.

Since the O_2 used for combustion was $12.0 + 1.9 = 13.9$ mols, while an excess of 7.5 was present, the per cent excess oxygen is

$$(7.5/13.9)100 = 54\%$$

This is, of course, identical with per cent excess air. This figure, however, makes no allowance for unburnt combustible, if present.

In computing excess air it must be remembered that the combustion reactions do not always, as in the case just quoted, complete themselves, some unburnt CO or H₂ perhaps remaining. Hence, some of the oxygen present as such is not actually in excess of that required for perfect combustion of the fuel gasified. An example follows.

Illustration 3. A flue gas is analyzed carefully in a mercury-filled Orsat. It contains 11.3% CO₂, 1.2% CO, 7.7% O₂, and 79.8% N₂. Find the per cent excess air.

Basis: 100 mols of gas as analyzed.

Gas	Mols	Atoms C	Mols O ₂
CO ₂	11.3	11.3	11.3
CO.....	1.2	1.2	0.6
O ₂	7.7	7.7
N ₂	79.8		
Total.....	100.0	12.5	19.6 O ₂ accounted for
79.8(21/79).....			21.2 O ₂ from air
O ₂ unaccounted for by analysis.....			1.6 O ₂ disappearance

Net H₂ burnt to H₂O, 2(1.6) = 3.2 H₂O from combustion

The oxygen present in the flue gas (7.7 mols) is not the true excess, since, by definition, complete combustion of carbon to CO₂ is required. This oxygen must be diminished by 0.6 mol, which is the amount required to burn the CO present to CO₂. The oxygen necessary for combustion is 12.5 mols for the carbon and 1.6 mols for the hydrogen, and the total oxygen entering the furnace is 21.2 mols. The per cent excess air (or oxygen) may be found in several ways:

$$(100) \frac{\text{unnecessary}}{\text{total} - \text{unnecessary}} = \frac{100(7.1)}{21.2 - 7.1} = 50.3\%$$

$$(100) \frac{\text{unnecessary}}{\text{necessary}} = \frac{100(7.1)}{12.5 + 1.6} = 50.3\%$$

$$(100) \frac{\text{total} - \text{necessary}}{\text{necessary}} = \frac{100(21.2 - 14.1)}{14.1} = 50.3\%$$

It will be noted that these are not independent solutions, but merely various arrangements of the same data.

In calculating the per cent excess air from the flue-gas analysis alone, it

must be assumed that no unburnt combustible leaves the system in the refuse. When such is not the case, due allowance must be made in the calculations (see page 105).

Air/fuel and flue-gas/fuel ratios. When the fuel contains negligible nitrogen and sulfur, and when losses of combustible matter such as soot, etc., are small, and when in addition it is known that there is a negligible amount of oxygen in the fuel, the flue-gas analysis alone is sufficient to enable one to determine the per cent excess air, the net-hydrogen/carbon ratio, and also the air/fuel and flue-gas/fuel ratios.

Illustration 4. A pure hydrocarbon gas at 70°F is burnt in a furnace giving a flue gas containing 10.8% CO₂, 3.8% O₂, and the rest nitrogen and inerts.

1. Calculate the atomic ratio, H/C, and from this the formula of the fuel.
2. If the combustion gases leave the furnace at normal pressure and 800°F, calculate the volumetric ratio, combustion gas/fuel gas.
3. If the furnace burns 200 lb of the fuel per hour, calculate the volume of combustion gases in cubic feet per minute.

Solution.

Basis: 100 mols dry flue gas as analyzed.

Gas	Mols	Atoms C	Mols O ₂
CO ₂	10.8	10.8	10.8
O ₂	3.8	3.8
N ₂	85.4		
Total.....	100.0	10.8	14.6 O ₂ accounted for
85.4(21/79).....			22.7 O ₂ from air
			8.1 O ₂ disappearance

Equivalent H₂ 2(8.1) = 16.2 mols H₂O

1. *Atomic ratio of H/C.*

$$2(16.2)/10.8 = 3 = \text{H/C atomic ratio}$$

The only hydrocarbons having H/C > 2 are saturated paraffins. Since these hydrocarbons have the general formula C_nH_{2n+2},

$$(2n + 2)/n = 3 \quad \therefore n = 2 \text{ and the fuel is C}_2\text{H}_6$$

2. *Ratio of combustion gases to fuel gas.* From the above table,

Mols of water vapor in flue gas = 16.2

Total mols combustion gases = 116.2

Since 100 mols of flue gas contain 10.8 atoms of carbon and since there are 2 atoms of carbon per mol of fuel gas, $(10.8/2) = 5.4$ mols of fuel are used per 100 mols of dry flue gas. Hence, the volumetric ratio of combustion products to fuel gas is

$$\frac{116.2(800 + 460)}{5.4(70 + 460)} = 51.1$$

3. *Cubic feet of combustion gases per minute.* The cubic feet of combustion gases per minute may be calculated by beginning with the given fuel rate of 200 lb of ethane per hour and proceeding to make a series of conversions, as follows:

$$200/60 = 3.33 \text{ lb ethane per minute}$$

Since the molecular weight of ethane is 30,

$$3.33/30 = 0.111 \text{ lb mol ethane per minute}$$

From the calculations under Part 2, the molal ratio of the wet combustion gases to the fuel is $116.2/5.4$, and therefore

$$0.111(116.2/5.4) = 2.39 \text{ lb mols wet gas per minute}$$

Since the pound-molecular volume at standard conditions (s.c.) is 359,

$$2.39(359) = 860 \text{ cu ft/min, s.c.}$$

Correcting this volume for temperature,

$$860(800 + 460)/492 = 2200 \text{ cu ft/min at } 800^\circ\text{F}$$

A series of steps such as the above is a simple and dependable method of arriving at the answer, but it suffers from the disadvantage of consuming more space and time than necessary. This is eliminated if the entire series of operations is compressed into a single line, as shown below:

$$200 \left(\frac{1}{60} \right) \left(\frac{1}{30} \right) \left(\frac{116.2}{5.4} \right) (359) \left(\frac{1260}{492} \right) = 2200 \text{ cu ft/min at } 800^\circ\text{F}$$

This method reduces slide-rule work, because it eliminates the necessity for reading and recording the settings of the rule at intermediate points in the calculation. The only setting that has to be recorded is the final one, 2200.

However, the use of the single-line method introduces a new difficulty. Experience shows that when the calculations are thus compressed the beginner frequently has a tendency to lose track of the units and to omit, inadvertently, some important factor in the long train of factors involved. Even the professional is not completely immune to such errors and finds it wise to have a device for checking results.

Perhaps the best way to ensure that the answer is in the proper units is to write the numerical figures in one line, expressing them as factors, and then write the units in the line below, placing the units of each factor directly beneath the corresponding numerical quantity. The following two lines illustrate the technique:

$$200 \left(\frac{1}{60} \right) \left(\frac{1}{30} \right) \left(\frac{116.2}{5.4} \right) (359) \left(\frac{1260}{492} \right) = 2200 \text{ cu ft/min at } 800^{\circ}\text{F}$$

$$\frac{\text{lb}}{\text{hr}} \left(\frac{\text{hr}}{\text{min}} \right) \left(\frac{\text{lb mol}}{\text{lb}} \right) \left(\frac{\text{mol}}{\text{mol}} \right) \left(\frac{\text{cu ft}}{\text{lb mol}} \right) \left(\frac{^{\circ}\text{R}}{^{\circ}\text{R}} \right) = \text{cu ft/min}$$

Cancellation of units where possible should leave behind, uncanceled, the units of the final answer.¹ Whenever there is the least uncertainty as to units, this means of checking should be used. The beginner will do well to use it consistently until he has convinced himself by practice that he can invariably keep track of the units without its aid.

The inadvertent omission of a factor is a danger that can be reduced by practice but never completely eliminated; the most competent of engineers slips occasionally. Accordingly, if one is to reap the advantages of time and space to be had from use of the single-line method and at the same time avoid costly errors, a device for keeping track of the operations is essential. The method here recommended and employed in subsequent calculations throughout the text is to arrange the series of steps in a horizontal sequence of factors, as shown below, with the *cumulative* result of the operations up to each point placed as a heading above each vertical column. The character of the conversion factors and ratios used

Lb C ₂ H ₆ per hr	Lb C ₂ H ₆ per min	Lb mols C ₂ H ₆ per min	Lb mols wet gas per min	Cu ft/min at s.c.	
200			116.2	359	1260
	60	30	5.4		492

= 2200 cu ft stack gas per minute, at 800°F

is ordinarily sufficiently obvious from the result achieved, so that matter descriptive of the ratios can be omitted.

Types of computational operations for which conversion factors or ratios are used. The simplicity of the conversion factors and ratios used in stoichiometric calculations of this sort should not be allowed to obscure the fact that they differ fundamentally in kind. Five important types are listed below. The student should learn to recognize them as they occur in computations. It will be found that all these types are illustrated in the preceding problem.

¹ In chemical engineering calculations the breakdown of the units into their ultimate dimensions is often unnecessary.

1. Change of units without change in dimensions; *e.g.*, conversion of feet to inches or to centimeters.

2. Change in the dimensions of the units in which a given quantity is expressed, involving the use of the numerical value of some fundamental physical property of the material in question; *e.g.*, a given quantity of liquid water at a given temperature can be expressed either in pounds or in cubic feet, its density serving as the conversion factor.

3. Transformations involving no change in either units or dimensions, which are based on fundamental general properties of the material; *e.g.*, use of the gas laws or of more general equations of state.

4. Transformations the validity of which depends upon the specific properties or condition of a given material; *e.g.*, relationships based upon the homogeneity of a given body or the composition of a given mixture.

5. Transformations based on the fundamental laws of stoichiometry; *e.g.*, material or element balances, the chemical laws of equivalent and combining weights, or heats of reaction. These may or may not involve changes in dimensions.

Illustration 5. The exhaust from a Diesel engine, using a high-grade hydrocarbon fuel oil, shows 10.2% CO₂, 7.9% O₂, and the rest nitrogen and inerts. The analysis was made with care in an Orsat, using mercury as the confining liquid in the measuring burette, and there is every reason to believe that the analysis is substantially correct. From these data, calculate

1. The weight ratio of hydrogen to carbon in the fuel oil
2. The per cent by weight of carbon in the oil
3. The pounds of dry air used per pound of oil burnt in the engine
4. The mols of exhaust gas discharged from the engine per pound of fuel oil burnt

Solution.

Basis: 100 mols dry exhaust gas.

Gas	Mols	Mols O ₂
CO ₂	10.2	10.2
O ₂	7.9	7.9
N ₂	81.9	
Total.....	100.0	18.1 O ₂ accounted for
81.9(21/79).....		21.8 O ₂ from air
		3.7 O ₂ disappearance

	<i>Lb</i>
H ₂ burnt, 2(3.7) = 7.4 mols.....	14.8
C burnt, 12(10.2).....	122.4
Total weight of fuel.....	137.2

1. *Weight ratio of hydrogen to carbon.*

$$(14.8/122.4) = 0.121$$

2. *Per cent by weight of C in fuel.*

$$(122.4/137.2)(100) = 89.2\% \text{ C}$$

3. *Pounds of dry air per pound of oil burnt.*

Mols N ₂ 81.9	Mols air 0.79	Lb air 29	137.2	= 21.9 lb air per pound oil
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4. *Mols of exhaust gas per pound of fuel burnt.*

$$(100 + 7.4)/137.2 = 0.783 \text{ mol per pound of fuel}$$

INTERRELATIONS OF FUEL AND FLUE-GAS ANALYSES

While the illustrations of the previous section show that in special cases it is possible to set up element balances on a furnace on the basis of the flue-gas analysis as the only quantitative data, it is always desirable to have complete analytical data on the fuel, particularly an ultimate analysis. In the absence of unburnt combustible matter the additional information contained in the ultimate analysis makes it possible to secure independent checks on the data of the gas analysis, thus furnishing evidence as to its degree of dependability. On the other hand, the ultimate analysis of liquid fuels is not usually made.¹ In cases of tar and soot formation, or the presence in the fuel of elements such as nitrogen, oxygen, and sulfur, data on the composition of the fuel is essential to any adequate analysis of the combustion operation.

Illustration 6. A hydrocarbon fuel oil is being burnt in an internal-combustion engine, which is running clean. Ultimate analysis of the oil shows 90.26% carbon and 9.45% hydrogen. Analysis of the combustion gases over mercury in the measuring burette shows 15.1% CO₂, 2.9% CO, 1.8% H₂, and 80.2% N₂. What light do these data throw on the combustion?

Discussion. The atomic ratio of net hydrogen to carbon in the fuel may be determined from the flue-gas analysis by the method of Illustration 5, with a correction for the presence of unburnt H₂ in the products of combustion. The ratio of the air supply to the theoretical quantity for complete combustion may also be computed.

¹ However, various correlations between physical properties and chemical composition are available.

Basis: 100 mols dry exhaust gas.

Gas	Mols	Atoms C	Mols O ₂
CO ₂	15.1	15.1	15.1
CO.....	2.9	2.9	1.45
H ₂	1.8		
N ₂	80.2		
Total.....	100.0	18.0	16.55 O ₂ accounted for
80.2(21/79).....			21.35 O ₂ from air
			4.8 O ₂ disappearance

H₂ burnt, $2(4.8) = 9.6$ mols ≈ 9.6 mols H₂O

Atomic ratio H/C, $(2)(9.6 + 1.8)/18 = 1.27$

Theoretical oxygen, $21.35 + 0.5(2.9) + 0.5(1.8) = 23.70$

Air supply, $(21.35/23.70)100 = 90.1\%$ of the theoretical

The determinations of carbon and hydrogen in the ultimate analysis of the fuel do not add up to 100%, but the difference is presumably due to minor errors in the analysis or to traces of other elements. The H/C ratio can also be obtained from the analysis of the fuel.

Basis: 100 lb of fuel oil.

Pound atoms of H, $9.45/1.008 = 9.37$

Pound atoms of C, $90.26/12.0 = 7.52$

Atomic ratio, H/C = $9.37/7.52 = 1.25$

This figure checks that obtained from the exhaust-gas analysis within the ordinary precision of the measurements, the check confirming the general dependability of the data.

To get the pounds of air per pound of fuel,

Basis: 1 lb of fuel oil.

Lb C	Atoms C	Mols O ₂	Mols air	
0.9026		21.35	100	29
	12	18.0	21	= 12.3 lb air

Instead of using oxygen as a measure of this air, one can use nitrogen:

Lb C	Atoms C	Mols N ₂	Mols air	
0.9026		80.2	100	29
	12	18.0	79	= 12.3 lb air

The percentage of water vapor in the wet exhaust gases is

$$100(9.6)/(100 + 9.6) = 8.8\%$$

assuming dry air used for combustion.

The following illustration emphasizes how relatively small may be the effect of moisture in air and fuel on the dew point¹ of the combustion gas.

Illustration 7. Using the data from Illustration 6, calculate the dew point of the exhaust gas on two different assumptions:

1. Assume that the air used for combustion had a dew point of 20°C (68°F).

2. Assume that the fuel analysis given is on a dry basis, but that the oil as fed to the engine contained, in fact, 9 weight per cent highly emulsified water, and that the air used for combustion had a dew point of 20°C.

Solution. Illustration 6, assuming dry air, showed that the exhaust gases would contain 8.8% by volume of water vapor. At normal barometer this is equivalent to a water-vapor pressure of 0.088 atm, which corresponds to a dew point of 43.6°C.

1. *Basis:* 100 mols of dry flue gas.

The mols of dry air per 100 mols of dry flue gas is $80.2(100/79) = 101.5$. Let y = mols of H₂O associated with 101.5 mols of dry air and $p_{\text{H}_2\text{O}}$ = the partial pressure of water vapor in the air.

Then, equating the mol ratio of water vapor to dry air computed from partial pressures to that computed from the number of mols of each,

$$\frac{p_{\text{H}_2\text{O}}}{P - p_{\text{H}_2\text{O}}} = \frac{y}{101.5}$$

in which P = the total pressure of the air used. Note that $p_{\text{H}_2\text{O}}$ and P may be in any units, such as atmospheres or millimeters of mercury, so long as both terms are in the same units. In this case, $P = 760$ mm and $p_{\text{H}_2\text{O}}$ at 20° = 17.5 mm. Solving the above equation, $y = 2.39$ mols. Hence, the partial pressure of water vapor in the exhaust gas = $(9.6 + 2.39)/(100 + 9.6 + 2.39) = 0.1073$ atm, and its dew point is 47.4°C.

2. Still using the basis of 100 mols of dry flue gas,

Lb C	Lb oil	Lb emulsi- fied H ₂ O	
18(12)	100	9	
	90.26	91	18

= 1.315 mols water emulsified in the fuel

Hence the partial pressure of water vapor in the combustion gas is

¹The dew point is the temperature at which the gas is saturated with water vapor, *i.e.*, the temperature at which the partial pressure of water in the gas is equal to the vapor pressure of water. In other words, it is the temperature at which "dew" can begin to form on cooling a vapor-gas mixture. Originally the term dew point was applied to condensation of moisture from air but now it is more broadly used to define the point at which, on cooling a vapor, liquefaction of the vapor begins, whether or not the vapor is by itself or in a mixture with noncondensable gas.

$(9.6 + 2.39 + 1.315)/(100 + 9.6 + 2.39 + 1.315) = 0.1174$ atm, corresponding to a dew point of 49.3°C .

Illustration 8. A high-grade fuel oil containing approximately 91% C and 9% H is burnt in a furnace that is well designed and well operated, giving a combustion gas, the Orsat analysis of which shows 12.4% CO_2 , 3.7% O_2 , and 83.9% N_2 and inerts. The air is substantially dry. What do these figures mean to you?

Discussion. A sketch of the process appears in Fig. 2-5.

The fuel analysis can be calculated from the flue-gas analysis by the technique outlined in the preceding problems. The atomic ratio H/C thus computed is 2.00, whereas the same ratio figured directly from the

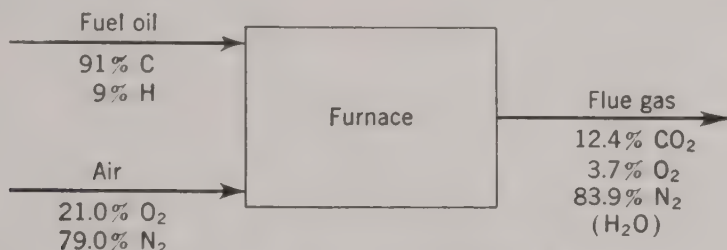


FIG. 2-5. Furnace of Illustration 8.

fuel analysis is 1.18. It is obvious that there must be some sort of error in the methods of sampling or analysis. Let it be granted that water was the confining liquid in the gas-measuring burette. This being the case, the most likely cause of the discrepancy is an error in the determination of CO_2 , due to absorption of CO_2 in the water (see p. 25).

A vital point to recognize is that in a case like this the apparent error in the flue-gas analysis does not necessarily make the test data worthless. To be sure, an error in the per cent CO_2 in one direction means that the percentages of O_2 and N_2 are off in the other direction, since because of the technique of analysis the total adds up to 100. However, study of the details of the Orsat technique shows that the ratio of O_2 to N_2 reported in the analysis is probably substantially correct, even if the absolute percentages are in error as a result of absorption of CO_2 in the confining liquid in the burette. This is because the amounts of O_2 and N_2 absorbed in the confining liquid are both too small to affect to a significant degree the amounts remaining after absorption of the CO_2 .

Choose as a basis of computation 100 lb of fuel oil. By carbon balance, the CO_2 in the flue gas is 91/12, or 7.58 mols. By hydrogen balance, the H_2O in the flue gases is 9/2.02, or 4.45 mols. Let x = mols of N_2 in the flue gases. By nitrogen balance, x is also equal to the mols of N_2 in the air supply. From the analysis of air, O_2 input is

$$x(21/79) = 0.266x \text{ mols}$$

From the flue-gas analysis, free O_2 in the combustion products is $0.037x/0.839 = 0.044x$ mols. An oxygen balance can now be written:

$$0.266x = 7.58 + 0.044x + (4.45/2)$$

Solving, $x = 44.2$ and $0.044x = 1.95$. The results may be tabulated as follows:

Basis: 100 lb of fuel.

Gas	Mols	Per cent
CO_2	7.58	14.1
O_2	1.95	3.6
N_2	44.2	82.3
Total water-free gas.....	53.73	100.0

The corrected value of CO_2 in the flue-gas analysis, it is evident, is somewhat higher than the value originally reported. This is the result one would expect if CO_2 absorption occurred in the burette in the original analysis. The fact that the correction turns out to be in the right direction strengthens the conjecture that this sort of an error in the CO_2 may be the explanation of the inconsistency of fuel and flue-gas analyses.

Illustration 9. The sulfur problem can be illustrated by a furnace using an otherwise high-grade petroleum fuel oil containing 5.2% sulfur. The flue gas is analyzed carefully over mercury without prior removal of SO_2 (which is therefore reported along with the CO_2), showing 13.9% CO_2 (+ SO_2), 0.4% CO , 0.1% H_2 , 2.4% O_2 , and 83.2% inerts. What is the analysis of the fuel?

Solution.

Basis: 100 mols dry flue gas.

Gas	Mols	C + S	O	H_2
$CO_2 + SO_2$	13.9	13.9	27.8	0.1
CO	0.4	0.4	0.4	
H_2	0.1	
O_2	2.4	4.8	
N_2	83.2	0.1
Total.....	100.0	14.3	33.0	
83.2(21/79)2.....	44.23	11.23
H_2 equivalent to O disappearance.....	
Total H_2 in fuel.....	11.33

$$\text{Ratio of } H_2/(C + S), 11.33/14.3 = 0.794$$

Now take as a basis 100 lb of the fuel oil. It contains 5.2 lb of sulfur. Call its hydrogen x . Its carbon is therefore $94.8 - x$. Hence its ratio of H_2 to $(C + S)$ is $\frac{x}{2.016} / \left(\frac{5.2}{32.07} + \frac{94.8 - x}{12} \right)$. Equating this to the value calculated above from the flue-gas data, 0.794, gives $x = 11.4$ weight per cent hydrogen, leaving 83.4 per cent carbon by difference.

It is well to note that the atomic ratio of sulfur to carbon in the fuel is only $(5.2/32.07)/(83.4/12) = 0.0233$. Hence, the SO_2 in the flue gas is only $0.0233(14.3)/(1.0233) = 0.33\%$, the CO_2 being $13.9 - 0.33 = 13.6\%$. In other words, the direct error involved is small, if the total shrinkage in alkali in the gas analysis is called CO_2 , even in a high-sulfur fuel such as this. Ignoring the sulfur completely in using the gas analytical data only raises net hydrogen in the oil to a trifle over 11.7%. This minor effect of a small amount of sulfur on the essential results of combustion calculations that are based on flue-gas data is the reason for the widely followed practice of ignoring the correction for sulfur.

High-nitrogen fuels. In the case of some gaseous and most liquid fuels, a small amount of nitrogen in the fuel may be neglected in the calculations. With some fuels, the nitrogen content is so high that this method cannot be followed. This is well illustrated in the combustion of producer gas in the problem below, in which the nitrogen from the fuel forms about 22% of the total nitrogen in the products of combustion.

Illustration 10. A producer gas contains 9.2% CO_2 , 0.4% C_2H_4 , 20.9% CO , 15.6% H_2 , 1.9% CH_4 , and 52.0% N_2 . When it is burnt, the products of combustion are found to contain 10.8% CO_2 , 0.4% CO , 9.2% O_2 , and 79.6% N_2 . Compute

1. The cubic feet of air used in the combustion of 1 cu ft of producer gas, both being at the same temperature and pressure
2. The per cent excess air used in combustion
3. The per cent of the nitrogen in the products of combustion which came from the producer gas

Solution.

Basis: 100 mols producer gas.

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	9.2	9.2	9.2
C_2H_4	0.4	0.8	0.8	
CO	20.9	20.9	10.45
H_2	15.6	15.6	
CH_4	1.9	1.9	3.8	
N_2	52.0			
Total.....	100.0	32.8	20.2	19.65

Basis: 100 mols dry combustion gas.

Gas	Mols	Atoms C	Mols O ₂	Mols N ₂
CO ₂	10.8	10.8	10.8	
CO.....	0.4	0.4	0.2	
O ₂	9.2	9.2	
N ₂	79.6	79.6
Total.....	100.0	11.2	20.2	79.6

One knows the mols of neither fuel gas nor air that went into the formation of 100 mols of dry combustion gas, which will be taken as the basis for calculation. The straightforward approach may be to use the algebraic method, calling the mols of fuel gas x and the mols of air y , and set up carbon and nitrogen balances.

$$0.328x = 11.2 \quad \text{whence } x = 34.15$$

$$0.52x + 0.79y = 79.6 \quad \text{whence } y = 78.3$$

Knowing the quantity and composition of producer gas and air, one may now compute the quantity of any element from either stream.

$$\text{O}_2 \text{ from air} = 78.3(21/100) = 16.44 \text{ mols}$$

$$\text{N}_2 \text{ from producer gas} = 34.15(52/100) = 17.75 \text{ mols}$$

1. *Cubic feet of air used per cubic foot of producer gas.* The molal ratio of air to fuel is $78.3/34.15 = 2.29$, which is also the ratio in cubic feet when both gases are at the same temperature and pressure.

2. *Per cent excess air.* Excess O₂ in combustion gas = $9.2 - 0.2 = 9.0$ mols.

$$100(9.0)/(16.44 - 9.0) = 121\% \text{ excess air}$$

3. *Per cent nitrogen in combustion gas which came from the producer gas.*

$$100(17.75/79.6) = 22.3\%$$

This problem may also be solved by an arithmetical method. The nitrogen in the combustion gas evidently comes from two sources, the producer gas and the air. On the other hand, the carbon was present originally in the producer gas only. The quantity of this latter gas must therefore be

$$11.2(100/32.8) = 34.15 \text{ mols producer gas}$$

Nitrogen/carbon ratio in producer gas is $52.0/32.8$. Similarly,

$$11.2(52.0/32.8) = 17.75 \text{ mols N}_2$$

in combustion gas from producer gas.

	<i>Mols</i>
Total N ₂ in combustion gas.....	79.6
N ₂ from producer gas.....	17.75
N ₂ from air.....	61.85
O ₂ from air, 61.85(21/79).....	16.44

The percentage of excess air and the percentage of nitrogen that came from the producer gas may now be computed as before.

The principle employed in this type of calculation should be studied carefully, because, as will appear later, it is frequently helpful in simplifying computations. In burning a fuel rich in nitrogen, the nitrogen in the flue gas is not a direct measure of the air employed for combustion, because a part of it comes from the fuel. On the other hand, it is possible, as shown above, to earmark and set aside the nitrogen from the fuel, the remainder coming from the air alone and being treated accordingly. The method of earmarking one or more portions of a constituent will be referred to repeatedly in later chapters.

One may compute the amount of excess air by another method. Take as a basis 100 mols of fuel. The air used to burn this is $2.29(100) = 229$ mols, and the oxygen in this air is $0.21(229) = 48.2$ mols. The oxygen needed to burn 100 mols of fuel is $32.8 + 20.2/2 - 19.65 = 23.25$ mols. Hence the excess of oxygen used over that required is $48.2 - 23.25 = 24.95$ mols and the percentage of excess is $100(24.95/23.25) = 107$ per cent. This is at variance with the value 121% previously calculated. The reason for the variance is not that the basis of computation has been changed from 100 mols of combustion gas to 100 mols of fuel gas (this was done purely for convenience) but that a different formula has been used for calculation. On page 37 three different formulas were given for finding the per cent excess air as follows:

$$100 \frac{\text{unnecessary}}{\text{total} - \text{unnecessary}} \quad (A)$$

$$100 \frac{\text{unnecessary}}{\text{necessary}} \quad (B)$$

$$100 \frac{\text{total} - \text{necessary}}{\text{necessary}} \quad (C)$$

In the previous problem the data came from one source, the flue gas. The solutions to the three formulas gave identical results because they simply became various arrangements of the same data. In this problem we have the compositions of the producer gas and of the combustion gas as separately made analyses, and therefore these data are independent. Consequently, the expression (total - unnecessary) may not equal (necessary) unless both sets of data are consistent.

When the first value of 121 % was obtained it will be noted that formula *A* was used, whereas 107 % was obtained by using formula *C*.

If we return to the basis of 100 mols of combustion gas, the value of 107 % will also be obtained if formula *C* is used.

	<i>Mols</i>
O ₂ from air was calculated as	16.44 (total)
O ₂ needed to burn producer gas, 34.15 (23.25/100)	7.95 (necessary)
O ₂ excess	8.49 (total - necessary)
100 (8.49/7.95) = 107 % excess air	

Further checking of the calculations shows that the ratios of fuel and of air to combustion gas were calculated by using carbon and nitrogen

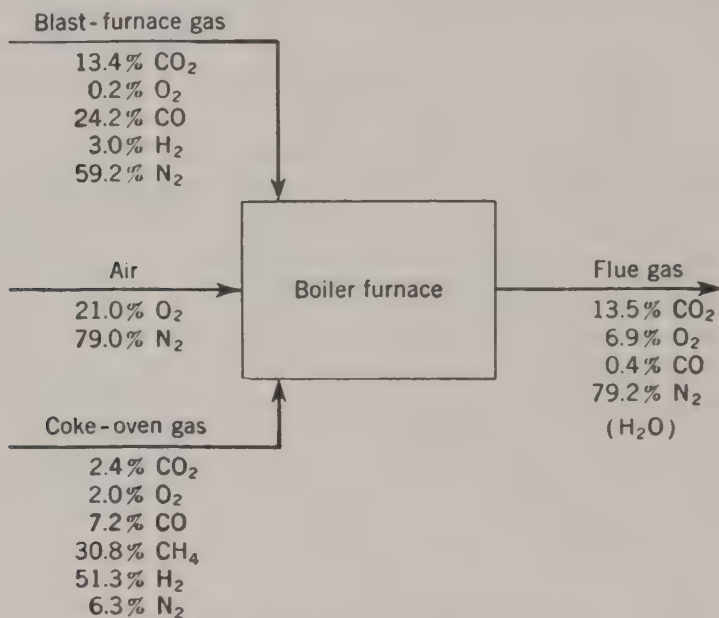


FIG. 2-6. Boiler furnace with mixed fuel.

balances. Since data are given on both hydrogen and oxygen, it would be highly desirable to check the results by balances on these two additional elements. However, since no data are given on the water content of the combustion gases, no check by direct balance on either of these elements is possible. As a substitute one can use a hydrogen balance to calculate the water in the combustion products and thus evaluate the oxygen disappearance. An oxygen balance can then be applied. But the result will be unsatisfactory because when the hydrogen and oxygen are brought into balance either the carbon or nitrogen or both of them will be out of balance.

The conclusion is that the producer-gas analysis and the combustion-

gas analysis are not consistent with each other. It must be evident to the reader by now that gases of combustion have a composition that is a unique function of the composition of the fuel, the air/fuel ratio, and the completeness of combustion. Any errors in sampling or in analysis will give results that do not "fit" the actual situation.

Mixed fuels. In an integrated chemical plant with a variety of operations, it sometimes happens that more than one type of fuel is used in a given furnace. When this is true, it is often desirable to calculate the ratio of the fuels by stoichiometrical methods, either as a check upon the ratio indicated by plant meters, or to determine the ratio, if metering facilities are not available on one or more of the fuel lines. The technique of calculation is shown by the succeeding illustration.

Illustration 11. The Buffalo Station of the M.I.T. School of Chemical Engineering Practice obtained the following data on the operation of a boiler furnace fired with a mixture of blast-furnace gas and coke-oven gas:

	Volume per cent					
	CO ₂	O ₂	CO	CH ₄	H ₂	N ₂
Coke-oven gas.....	2.4	2.0	7.2	30.8	51.3	6.3
Blast-furnace gas.....	13.4	0.2	24.2	3.0	59.2
Flue gas.....	13.5	6.9	0.4	79.2

Calculate

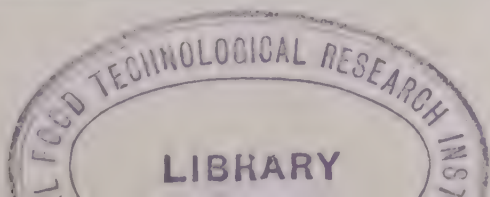
1. The ratio of blast-furnace gas to coke-oven gas
2. The per cent excess air used

Solution. Visualization of the process is aided by the sketch of Fig. 2-6.

It is obvious that the first step is to restate each of the analyses in terms of each element present. This has been done in the following tables:

Basis: 100 mols coke-oven gas.

Gas	Mols	C	H ₂	O	N ₂	Theoretical O ₂
CO ₂	2.4	2.4	4.8
O ₂	2.0	4.0	...	-2.0
CO.....	7.2	7.2	7.2	...	3.6
CH ₄	30.8	30.8	61.6	61.6
H ₂	51.3	...	51.3	25.7
N ₂	6.3	6.3
Total.....	100.0	40.4	112.9	16.0	6.3	88.9



Basis: 100 mols blast-furnace gas.

Gas	Mols	C	H ₂	O	N ₂	Theoretical O ₂
CO ₂	13.4	13.4	...	26.8		
O ₂	0.2	0.4	-0.2
CO.....	24.2	24.2	...	24.2	12.1
H ₂	3.0	3.0	1.5
N ₂	59.2	59.2	
Total.....	100.0	37.6	3.0	51.4	59.2	13.4

Basis: 100 mols dry flue gas.

Gas	Mols	C	H ₂	O	N ₂	Excess O ₂
CO ₂	13.5	13.5	...	27.0		
O ₂	6.9	13.8		
CO.....	0.4	0.4	...	0.4		
N ₂	79.2	79.2	
Total.....	100.0	13.9	0.0	41.2	79.2	
Excess O ₂ , 41.2/2 - 13.9.....	6.7

Solution of the problem evidently depends on the choice of a basis and unknowns, followed by application of balances on the various elements. A wide variety of mathematically correct choices exists. However, some choices of basis and unknowns lead to involved calculations, while others do not. In general, the manipulations are simplified in this type of problem, if one will choose as basis a convenient quantity of one of the streams and let the total number of mols in each of the other streams be unknown. Let the basis be 100 mols of coke-oven gas and let the unknowns be

x = mols of blast-furnace gas

y = mols of air

z = mols of dry flue gas

w = mols of H₂O in the flue gases

Balances on the individual elements can now be written:

$$\text{C balance: } 0.376x + 40.4 = 0.139z$$

$$\text{H}_2 \text{ balance: } 0.030x + 112.9 = w$$

$$\text{O balance: } 0.514x + 16.0 + 0.42y = 0.412z + w$$

$$\text{N}_2 \text{ balance: } 0.592x + 6.3 + 0.79y = 0.792z$$

Solving,

$$x = 503 \text{ mols of blast-furnace gas}$$

$$z = 1652 \text{ mols of dry flue gas}$$

1. *Ratio of blast-furnace gas to coke-oven gas.*

$$503/100 = 5.03$$

2. *Per cent excess air used.* Theoretical O_2 is $88.9 + 5.03(13.4) = 156.3$ mols per 100 mols coke-oven gas. Per cent excess air is

$$100(6.7)(1652/100)/156.3 = 71\%$$

PROBLEMS

1. If dry hydrogen gas at atmospheric pressure is burnt completely in a furnace with 32% excess air, calculate the Orsat analysis of the flue gas from this furnace.

Ans. 6% O_2 , 94% N_2 .

2. If moist hydrogen containing 4% of water by volume is burnt completely in a furnace with 32% excess air, calculate the Orsat analysis of the resulting flue gas.

Ans. 6% O_2 , 94% N_2 .

3. Calculate what should be the Orsat analysis resulting from the complete combustion with 100% excess air of

(a) Ethane, C_2H_6 .

Ans. 6.3% CO_2 , 11.0% O_2 , 82.7% N_2 .

(b) Naphthalene, $C_{10}H_8$.

Ans. 8.9% CO_2 , 10.7% O_2 , 80.4% N_2 .

4. An automobile engine is being operated with pure methyl alcohol, CH_3OH , using 10% excess air over that necessary for theoretical combustion, and securing substantially complete combustion of the fuel. A sample of the exhaust gases is removed from the exhaust pipe and carefully analyzed in an Orsat. What analysis would you expect to get?

5. Pure formaldehyde gas, CH_2O , is burnt completely in air, using 50% excess.

(a) What should be the Orsat analysis of the combustion gas?

(b) What should be the Orsat analysis of the combustion gas if, instead of using excess air, only enough were used to burn all the hydrogen to water, 25% of the carbon to CO_2 , and the remaining 75% to CO, the combustion being so conducted that no oxygen gas whatever is left remaining in the combustion products?

6. Assume that in the operation of the engine of Prob. 4, using pure methyl alcohol as fuel as there stated, the air supply is reduced below the theoretical value to a point such that 90% of the carbon in the fuel burns to CO_2 and the remaining 10% to CO; assume, furthermore, that under these conditions the hydrogen in the gaseous combustion products is 40% of the CO in them, the oxygen being all consumed.

Calculate the following:

(a) The Orsat analysis that you would expect to find for the gases from the exhaust pipe.

(b) The pounds of dry air required per pound of fuel burnt.

(c) The cubic feet of dry air that must be supplied to the engine per pound of fuel burnt, on the assumption that the barometer is normal and the air temperature is $70^\circ F$.

(d) The volume of exhaust gases per pound of fuel burnt, if these leave the engine at $960^\circ F$.

7. An automobile engine is supplied with a gasoline that is found by analysis to contain 88% carbon and 12% hydrogen. It is operated at normal barometer.

(a) Calculate the Orsat analysis of the exhaust-pipe gases, the pounds of dry air required per pound of fuel, the volume of this air at $60^\circ F$, and the volume of the combustion gases at $1000^\circ F$, granting complete combustion with theoretical dry air.

(b) Repeat (a), granting combustion with 90% of the theoretical air under condi-

tions such that the oxygen will be completely eliminated and the molal ratio of CO to H_2 in the combustion gases will be 2:1.

8. An aviation engine using high-octane gasoline for fuel flies at an altitude where the barometric pressure is 430 mm Hg abs. The air is practically dry and at a temperature of $18^\circ F$. The exhaust gases leave the engine at $1000^\circ F$. During flight a sample of the engine exhaust gases is obtained under these conditions and is taken to the ground for analysis. The Orsat analysis, with mercury as the confining liquid in the burette, is conducted at $20^\circ C$ and 750 mm Hg and shows 13.39% CO_2 , 1.67% O_2 , and 84.94% N_2 . For information on the design of a gas turbine supercharger driven by these exhaust gases, calculate the cubic feet of exhaust gases (under the conditions they leave the engine) per cubic foot of air entering the air intake. *Ans.* 3.28 cu ft.

9. A small experimental laboratory furnace is operated conventionally with a variety of special fuels. The combustion gases are analyzed carefully over mercury by conventional techniques, and there is no reason to question the substantial dependability of the analytical results. What is the significance to you of the following data, collected in the course of this work?

- (a) A gaseous fuel gives a combustion gas containing 6.2% CO_2 , 4.6% O_2 , and the rest nitrogen (and inerts).
- (b) A water-white, anhydrous liquid fuel gives a combustion gas containing 16.2% CO_2 , 4.8% O_2 , and the rest N_2 .
- (c) A pure, solid organic compound gives 15.46% CO_2 , 3.09% O_2 , and the rest N_2 .

10. A relatively pure saturated hydrocarbon gas is being burnt with air in a small furnace. A sample of the flue gas is taken, and a portion is subjected to analysis in a standard Orsat apparatus. The data obtained are as follows:

	<i>Milliliters</i>
Initial volume of sample.....	100.0
After caustic absorption.....	92.6
After pyrogallol absorption.....	87.1
After cuprous chloride absorption.....	83.4

On the basis of this analysis,

- (a) What is the per cent excess air?
- (b) What is the atomic ratio of hydrogen to carbon in the original fuel? What is the hydrocarbon being burnt?
- (c) How many cubic feet of dry flue gas (measured at standard conditions) are formed per pound of hydrocarbon consumed?

11. The combustion gases from an industrial furnace using a hydrocarbon fuel and dry air enter the stack at normal barometric pressure and $375^\circ F$ and have the following Orsat analysis: 12.2% CO_2 , 3.1% O_2 , 1.2% CO, and 83.5% N_2 .

Determine the following:

- (a) The per cent excess air.
- (b) The volume of gases entering the stack, expressed as cubic feet per pound of carbon burnt in the furnace.
- (c) The dew point of the stack gases.
- (d) The atomic ratio of hydrogen to carbon in the fuel.
- (e) The mols of stack gas per atom of carbon burnt.

12. A 12-ml sample of a mixture of ethane and dry air is added at constant pressure to 100 ml of dry air, and the resulting mixture is exploded. The exhaust gases are passed through concentrated sulfuric acid and a sodium hydroxide solution in succession and then to a measuring bulb where the final volume is found to be 98.5 ml. What is the per cent composition of the original 12-ml sample? *Ans.* 25% C_2H_6 .

13. Mixtures of the hydrocarbons ethylene and propylene are to be analyzed by carrying out a slow combustion with excess oxygen. Formulate a simple relationship based on the usual data collected in the above procedure, so that a trained technician with no background in stoichiometry can calculate the per cent of propylene in the original hydrocarbon gas sample.

NOTE: The data collected in such a procedure involve the volume of the hydrocarbon gas sample added to a given volume of pure oxygen. The volume after combustion is measured and then after KOH absorption the volume is again measured.

14. A waste gas from a petroleum refinery is analyzed as follows: A sample of exactly 100 ml is found to shrink to 91.8 ml on absorption in lead acetate solution; to 90.2 ml in KOH; to 88.0 ml in pyrogallate; to 81.2 ml in strong sulfuric; and no further shrinkage is observed in cuprous chloride. The 81.2 ml of gas after sulfuric absorption shows no shrinkage over palladium black. One-fourth of the remaining gas, namely, 20.3 ml, is mixed with 70 ml of pure O_2 and exploded. The volume after explosion is 53.2 ml; this shrinks to 27.5 ml in KOH and to 4.2 ml in pyrogallate. A second sample, likewise exactly 100 ml, is analyzed in the same way (the absorptions checking the first sample, except that the absorption in sulfuric is omitted), and exactly one-fourth of the gas now remaining, namely, 22 ml, is mixed with 70 ml of pure O_2 and exploded. The volume after explosion is 50.0 ml, which shrinks to 17.8 ml in KOH and to 4.2 ml in pyrogallate. Calculate the analysis of the gas on a percentage basis as completely as possible from these data.

15. A chemical manufacturer produces ethylene oxide by burning ethylene gas with air in the presence of a catalyst. If the conditions are carefully controlled, a substantial fraction of the ethylene is converted to ethylene oxide, while some ethylene remains unconverted and some is completely oxidized to form carbon dioxide and water. Formation of carbon monoxide is negligible. After the gases leave the reactor, they are passed through an absorber, in which the ethylene oxide is removed. A typical Orsat analysis of the gases leaving the absorber is as follows: 9.6% CO_2 , 3.0% O_2 , and 6.4% ethylene. Of the ethylene entering the reactor, what per cent is converted to ethylene oxide?

16. The off-gas from a phosphate-ore reduction furnace, analyzing 7% P_4 , 90% CO, and 3% N_2 on a gas volume-per cent basis, is burned with air under conditions favoring selective oxidation of the phosphorus. A sample of the flue gases from the burner is withdrawn from the stack and cooled. The oxides of phosphorus, which precipitate on cooling, are separated from the remaining gas, and the latter is analyzed in an Orsat apparatus. The results show 0.8% CO_2 , 22.4% CO, 8.7% O_2 , and 68.1% N_2 . It may be assumed that the amount of P_4 in the flue gases is negligible and that the phosphorus in the flue gases exists partly as P_4O_6 and partly as P_4O_{10} . Of the CO entering the burner, what per cent is oxidized to CO_2 ? Of the P_4 entering the burner, what per cent is oxidized to P_4O_{10} ?

17. A furnace uses a producer gas of the following analysis: 5.3% CO_2 , 21.1% CO, 15.3% H_2 , 1.0% CH_4 , and 57.3% N_2 . The flue gas contains 14.1% CO_2 , 2.3% O_2 , and 83.6% N_2 . Both analyses were conducted in an Orsat apparatus with mercury as the confining liquid and were made by a skilled technician.

(a) Assuming that the analyses are truly representative of the fuel and flue gas, calculate, by two different methods, the per cent excess air used in the furnace.

(b) A check on the history of the gas samples reveals that although they were analyzed over mercury, each of the two samples was brought from the plant to the laboratory in a container with water as the confining liquid. Recalculate the per cent excess air in the light of this discovery.

18. A producer gas is burned under a boiler with 20% excess air. The analysis of

the producer gas, determined by a thoroughly reliable technique, is 2.0% CO_2 , 28.0% CO , 2.0% O_2 , 10.4% H_2 , and 57.6% N_2 . Between the point at which the flue gas enters the stack and the point at which the flue-gas sample is taken, a certain amount of air leaks into the stack. The Orsat analysis of the diluted flue gases, determined with water as the confining fluid, is 4.6% CO_2 , 3.0% CO , 10.8% O_2 , and 81.6% N_2 .

(a) What is the air leakage in mols per 100 mols of dry fuel fired?

(b) Compute the analysis of the dry flue gas before dilution.

19. A rocket motor uses pure nonane (C_9H_{20}) as a fuel and pure hydrogen peroxide as an oxidant. During a 10-min test period the fuel meter shows that the average rate of consumption of nonane is 119 lb/min. The hydrogen peroxide meter fails to function. However, the exhaust gas is collected at atmospheric pressure (760 mm Hg) and cooled to 20°C . During the 10-min period 2701 lb of liquid is obtained. This liquid is analyzed and found to contain 0.172% CO_2 by weight. The vapor pressure of water at 20°C is 17.5 mm Hg.

During the course of the test a sample of the exhaust gas is withdrawn through a sample line and cooled to atmospheric temperature (85°F), and the gas phase is analyzed in an apparatus in which water is used as the confining fluid in the measuring burettes. The observed volume of the gas subjected to analysis is 96.7 ml, the volume after passing through KOH solution is 84.7 ml, the volume after passing through CrCl_2 solution is 84.7 ml, and that after passing through acidified Cu_2Cl_2 solution is 44.86 ml. To the residual 44.86 ml is added 200.0 ml of air. This mixture is subjected to slow combustion over a hot platinum filament. After cooling of the gas, the volume is 177.57 ml. The gas is then passed through the KOH solution once more; no shrinkage is observed.

Estimate the composition of the wet exhaust gas and the molal ratio of peroxide to nonane.

Chapter 3

ENERGY BALANCES AND EQUILIBRIUM

In the technology of fuels, the over-all objective is normally the production and utilization of heat. Hence, material balances of the type discussed in the preceding chapter are usually a preliminary to energy computations. The latter are employed to test the dependability of data obtained in the plant, to check the efficiency of utilization of heat in a process, and for design purposes. At the same time there arise questions as to the potentialities of heat exchange and recovery, which can only be answered in the light of the temperature levels at which heat is released or absorbed and the temperature differences available as the driving force in heat-transfer equipment. These problems involve limitations imposed by physical and chemical equilibria. Therefore, the present chapter deals with both the energy relationships encountered in the recovery of heat and the related problems of physical and chemical equilibria.

It will be best to start with certain relatively simple problems involving physical-heat effects only. This will make it possible to grasp the principles underlying these physical changes and to master the techniques of computation involved in handling them. This, in turn, will aid in allowing for them in those more complicated situations in which the effects of chemical interaction are superimposed upon them.

RECOVERY OF HEAT

As will be brought out in succeeding chapters, the recovery of heat from combustion gases is of great importance in many chemical processes, partly because of the resultant economies in fuel, but also because in many cases the proper utilization of what would otherwise be waste heat is absolutely essential to successful operation.

Heat exchange. In the operation of a continuous adiabatic heat exchanger involving two steadily flowing streams, the heat given up by one stream must equal that picked up by the other, not only in the unit as a whole but in every individual section of it, however large or small.¹

¹ This assumes no heat flow along the structure of the exchanger itself (*e.g.*, through the metal of the unit) in a direction parallel to that of movement of the flowing streams.

Furthermore, the temperature of the stream giving up heat must, at every point in the exchanger, be higher, at least differentially, than the temperature of the heat-accepting stream at the corresponding point, since this sort of temperature difference is the driving force essential for the transfer of the heat. The two effects are interrelated by the fact that the temperature of each stream at any given point is determined by the heat it has lost or gained up to that point.¹ Meanwhile, the rate of transfer of heat is determined by the temperature difference between the two streams, together with other important factors in construction and operation of the unit.

As will be made evident in succeeding chapters, there are many types of equipment in which the performance is governed by a heat balance, applying to the unit as a whole and also to each individual zone, and where the flow of heat is restricted by the necessity of maintaining at all points a unidirectional temperature difference. Because heat exchange offers the simplest application of the principle of driving forces, it can serve as an ideal introductory illustration.

In any process of interchange of sensible heat between two bodies, the dominant factors which set absolute limits to the operation are the initial temperatures of the bodies and their heat capacities. For example, if the total heat capacity of the cold body is small compared to that of the hot, it is obvious that transfer of a relatively small amount of heat will raise the temperature of the cold body nearly to that of the hot, with little drop in temperature of the latter, thus blocking further flow of heat. It is also clear that these same factors determine the temperature levels and hence the temperature differences at each stage in the process. Because the *rate* of heat transfer at each point in the equipment is a function of the temperature difference at this point, these factors therefore determine the total heat-transfer capacity of any given type of equipment used for the operation. What follows is a discussion of continuous, steady-flow heat exchange, limited to the heat-balance and temperature-difference phases of the problem.

If the specific heats of the hot and cold streams are almost constant, or can be expressed as simple functions of temperature, an analytical approach is entirely adequate. However, even in such simple cases the use of graphical methods brings out certain points not emphasized by algebra. In more complicated situations, involving phase changes or considerable variation of specific heat with temperature level, graphs are almost indispensable. Because of their more general utility, graphical methods receive the major emphasis in succeeding sections.

¹ Either temperature or heat exchanged may be taken as the independent variable at will.

Parallel-flow heat exchange. In the recovery of heat perhaps the simplest type of equipment to visualize is a continuously operating exchanger, in which the hot and cold streams flow through the apparatus in parallel, *i.e.*, side by side and in the same direction (see Fig. 3-1). With this arrangement of flow, the temperature difference between the hot and cold streams is large at the point where the two streams enter, and therefore the initial rate of heat transfer between the two streams is relatively high. Because of this characteristic, parallel flow is employed under circumstances where it is important to cool reaction products extremely rapidly, *e.g.*, through a range of temperatures in which undesirable reactions will otherwise occur. The energy and thermal equilibrium relationships are illustrated by the following example.

Illustration 1. It is desired to cool very rapidly the exit gases from an ammonia-oxidation unit (see page 226), in order to prevent any appreciable decomposition of NO to N_2 and O_2 . At the same time, heat is to be recovered by employing the incoming air to the unit as the cooling medium in a parallel-flow heat exchanger. The analysis of the exit gases is 9.1% NO, 4.7% O_2 , 69.5% N_2 , and 16.7% H_2O , and they leave the catalyst chamber at 1700°F . Air is supplied to the unit in the ratio of 0.87 mol of dry air per mol of exit gas and will enter the exchanger at an average temperature of 60°F .

1. If it were possible by some means to cool the gases to 60°F , recovering all the sensible heat, how much heat would be thus recovered, in Btu per 100 lb mols of gas?

2. If it were similarly possible to heat the air to 1700°F , how much heat would the air take up, expressed in the same units, on the same basis?

3. Granting that one has an adiabatic heat exchanger, what is the relation between the quantity of heat transferred from one stream to the other and the resulting temperatures of the two streams at any specific section of the exchanger?

Solution. The exchanger may be represented by the simple diagram of Fig. 3-1.

As a basis of computation, choose 100 lb mols of exit gas. The mols of NO, O_2 , etc., in the gas will then be numerically equal to the percentages in the gas analysis, shown in Fig. 3-1. On this basis, the mols of O_2 in the air will be $87(0.21) = 18.3$, and the mols of N_2 in the air will be $87 - 18.3 = 68.7$.

1. Focusing attention first on the hot exit gases, if these are cooled by some means to 60°F , the heat given up is simply the sum of the sensible-heat contents¹ at 1700°F of the various constituents, relative to 60°F . For example, the sensible-heat content of the NO above 60°F is obtained

¹ The *heat content* is also known as the *enthalpy*. Both terms are used in this book.

by reading the value of $Mc_{p,av}^\circ$ at 1700°F from Fig. 1-3 and multiplying the figure read from the plot, 7.7, by the number of mols of NO and the difference between 1700° and 60°. Thus, $7.7(9.1)(1640) = 115,000$ Btu. The calculations for the various constituents are summarized in the table below.

Constituent	Mols	$Mc_{p,av}^\circ$ at 1700°F	(Mols)($Mc_{p,av}^\circ$)(1640)
NO	9.1	7.7	115,000
O ₂	4.7	7.9	61,000
N ₂	69.5	7.5	855,000
H ₂ O	16.7	9.1	249,000
Total sensible-heat content at 1700°F. . . .			1,280,000 Btu

2. The amount of heat which the air can take up in rising in temperature from 60°F to 1700°F is calculated in exactly the same way, remembering that there are 87 mols of this air, of which 18.3 mols are oxygen and

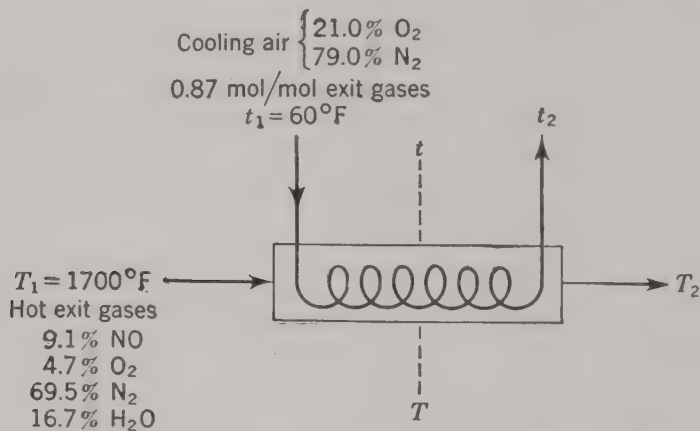


FIG. 3-1. Parallel-flow heat exchanger of Illustration 1.

the rest nitrogen. The result is 1,075,300 Btu. It will be seen that the heat-absorption capacity of the air is less than the heat-carrying capacity of the product gas by $1,280,000 - 1,075,300 = 204,700$ Btu. In other words, there is not enough heat-absorbing capacity in the air to cool the product gases completely to 60°F under any conditions of heat transfer whatever.

3. To determine the relation between the amount of heat transferred from the hot gas to the air and the temperatures of the hot and cool streams, let the temperature of the air at any section of the exchanger, such as that represented by the dotted line in the diagram, be equal to t , and let the temperature of the gas at the same section be T , both expressed in degrees Fahrenheit.

Now consider that portion of the exchanger between the inlet and the section at the dotted line and apply an energy balance to that portion. Since no heat is lost to the surroundings, all heat given up by the gas in cooling from 1700°F to T is absorbed by the air in being heated from 60°F to t . Let the heat thus transferred, in Btu, be designated as Q .

The relationship between t and Q is obtained from the fact that the heat absorbed by the air in being heated from 60°F to t is the sensible-heat content of the air at t relative to 60°F. For example, the value of Q when $t = 600^\circ\text{F}$ is computed as follows. At 600°F, the value of $Mc_{p,\text{av}}^\circ$ read from the O_2 curve of Fig. 1-3 is 7.3. The sensible-heat content of the O_2 in the air is obtained as the product of $Mc_{p,\text{av}}^\circ$ with the number of mols of O_2 and the difference between 600° and 60°F. Thus,

$$7.3(18.3)(540) = 72,000 \text{ Btu}$$

By a similar calculation, the sensible-heat content of the N_2 in the air is $7.0(68.7)(540) = 260,000$ Btu. The calculations by which values of Q are obtained for a number of different values of t are summarized in Table 3-1. Note that this relation between Q and t is a unique function

TABLE 3-1. HEAT TRANSFERRED FROM HOT GAS TO AIR AS A FUNCTION OF AIR TEMPERATURE

<i>A</i>	t	200	400	600	800	1000	1200	1400
<i>B</i>	$t - 60$	140	340	540	740	940	1140	1340
<i>C</i>	$Mc_{p,\text{av}}^\circ$ at t : O_2	7.1	7.2	7.3	7.4	7.5	7.7	7.8
<i>D</i>	N_2	7.0	7.0	7.0	7.1	7.2	7.3	7.3
<i>E</i>	$18.3(C)(B)$	18,000	45,000	72,000	100,000	129,000	161,000	191,000
<i>F</i>	$68.7(D)(B)$	67,000	164,000	260,000	361,000	465,000	572,000	673,000
<i>G</i>	$E + F = Q$	85,000	209,000	332,000	461,000	594,000	733,000	864,000

of the quantity and properties of the air stream, completely independent of other factors in the problem.

The relation between T and Q is determined by the fact that the heat given up by the hot gas in cooling from 1700°F to T equals the sensible-heat content of the gas at 1700°F, relative to 60°F, minus the sensible-heat content at T , relative to the same base temperature.

Computations of the sensible-heat content at T and the corresponding values of Q , for several different values of T , are given in Table 3-2. The results, like those for the air, are uniquely dependent on the amount and the properties of the hot-gas stream alone.

These results give the desired relation between the amount of heat transferred from the hot gases to the air and the temperatures of the two streams, best expressed graphically in Fig. 3-2. Examination of this figure will make it clear that any vertical line between the two curves such as AB corresponds to a heat balance from the gas-inlet end of the

exchanger up to the section in question. This is because the upper curve represents the heat given up by the hot gas and the lower curve, the heat picked up by the cold air; in an adiabatic exchanger the two must be equal. On the diagram, the vertical distance between the two curves at any particular value of the heat transferred is the temperature difference between the two gas streams at the point in question in the exchanger. The location of T_2 and t_2 , the temperatures at which the gas and air, respectively, leave the outlet end of any given exchanger, depends on the area available in the exchanger for transfer of heat and the coefficients of heat transfer. For a given type of exchanger, the coefficients of heat transfer will be approximately constant, and the significant variable will be the area available for heat transfer. Thus, if the area is relatively small, the amount of heat transferred will be small, *e.g.*, 200,000 Btu. In

TABLE 3-2. HEAT TRANSFERRED FROM HOT GAS AS A FUNCTION OF GAS TEMPERATURE

A	T	1600	1400	1200	1000	800	600
B	$T - 60$	1540	1340	1140	940	740	540
C	$Mc_{p,av}$ at T : NO.....	7.7	7.6	7.5	7.4	7.3	7.2
D	O ₂	7.8	7.8	7.7	7.5	7.4	7.3
E	N ₂	7.4	7.3	7.3	7.2	7.1	7.0
F	H ₂ O.....	9.1	8.9	8.7	8.6	8.4	8.3
G	9.1(C)(B).....	108,000	93,000	78,000	63,000	49,000	35,000
H	4.7(D)(B).....	57,000	49,000	41,000	33,000	26,000	19,000
I	69.5(E)(B).....	791,000	680,000	579,000	470,000	365,000	263,000
J	16.7(F)(B).....	234,000	199,000	166,000	135,000	104,000	75,000
K	$G + H + I + J = \text{sens.}$ heat content at T	1,190,000	1,021,000	864,000	701,000	544,000	392,000
L	1,280,000 - $K = Q$	90,000	259,000	416,000	579,000	736,000	888,000

this case, line AB in Fig. 3-2 shows that the exit temperature of the gas will be 1470°F, while that of the air will be 390°F. If a somewhat larger exchanger is employed, resulting in a heat transfer of 400,000 Btu, then $T_2 = 1220^\circ\text{F}$ and $t_2 = 700^\circ\text{F}$ (line CD). However, as larger and larger exchangers are employed, the values of T_2 and t_2 approach each other, reducing the temperature difference available as the driving force for transfer of heat. If heat transfer from the gas to the air is to take place, the temperature of the gas must exceed that of the air. Hence, no matter how large the exchanger, it is never possible to reach the condition at which the gas and the air leave the exchanger at identically the same temperature. The condition at which $T_2 = t_2$ is thus the limiting case, attained only by using an exchanger the area of which is indefinitely large. As is seen from Fig. 3-2, this corresponds to a temperature of 990°F and a heat removal of 590,000 Btu. Therefore, the maximum percentage of the sensible heat of the gas above 60°F that can be recovered under the conditions specified is $(590,000/1,280,000)100 = 46.1\%$.

Figure 3-2 can thus be used to determine the over-all performance of any given exchanger, *i.e.*, the outlet temperatures of the two streams. Once these have been established, it also shows the relations between temperatures, temperature differences, and the amount of heat transferred up to any given section within the exchanger.

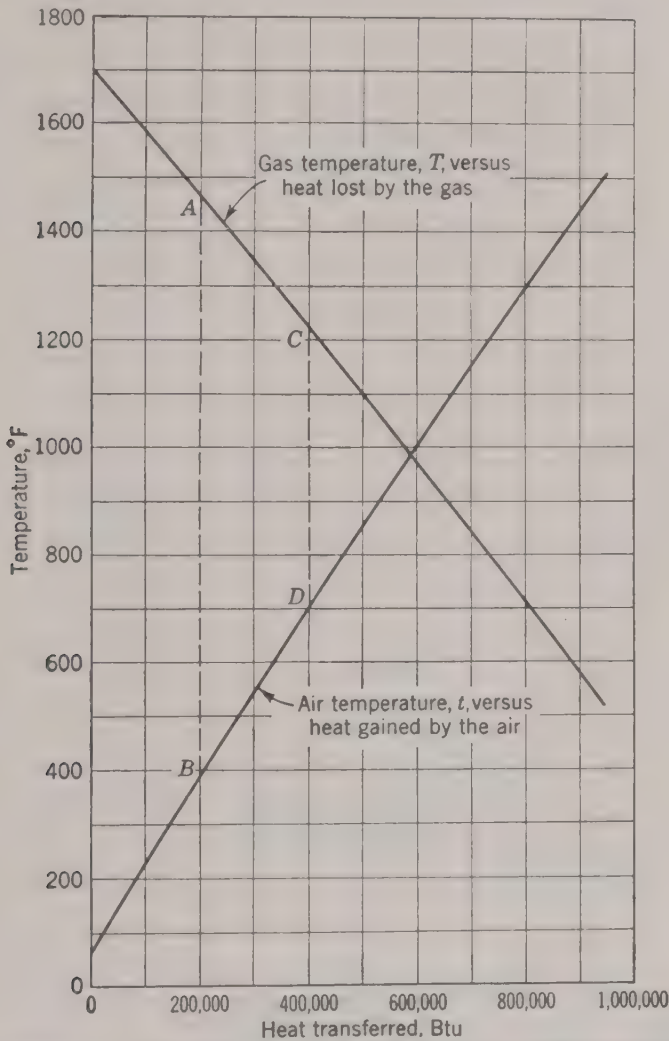


FIG. 3-2. Temperature distribution in parallel-flow heat exchanger of Illustration 1. Basis: 100 lb mols of hot exit gases.

Any vertical line on the diagram represents a heat balance only. This is true to the right of the intersection of the two curves as well as to the left. However, for a parallel-flow exchanger, conditions to the right of the intersection are impossible of attainment because beyond the intersection point they would represent flow of heat from a low temperature level to a higher one. Such conditions, although still compatible with

an energy balance, would violate the requirements of thermal equilibrium.

It has been pointed out that each curve of Fig. 3-2 is a unique function of its stream. As long as the compositions and the relative quantities of the two streams remain unchanged, advantage can be taken of this fact

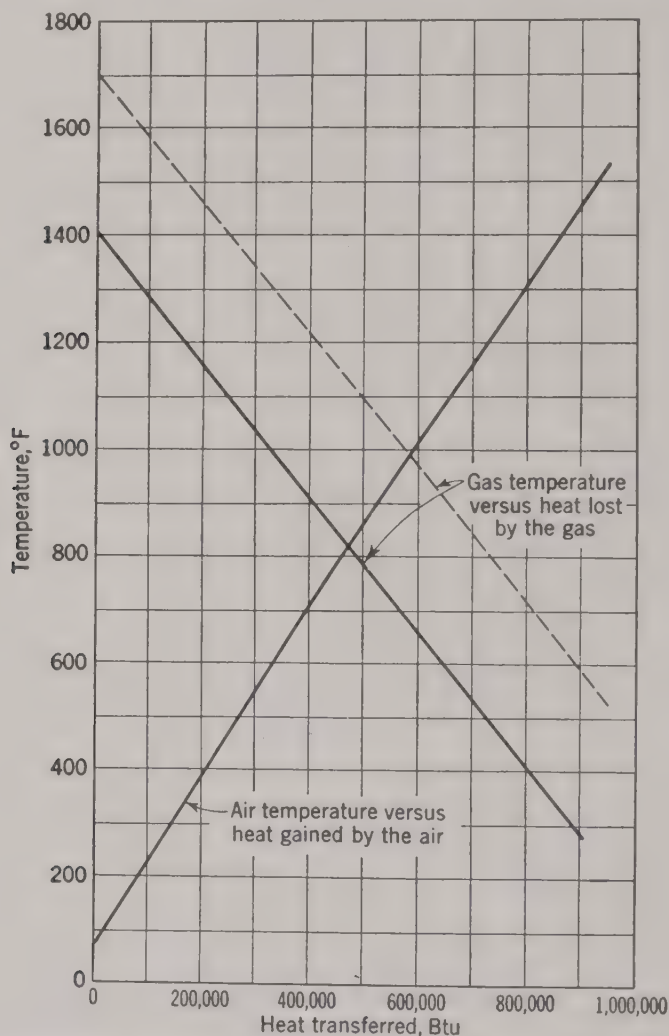


FIG. 3-3. Temperature distribution in parallel-flow heat exchanger of Illustration 1. Effect of a change in T_1 . Basis: 100 lb mols of hot exit gases.

to solve a variety of problems. Thus, assume that because of some change in operating conditions the hot gases of this problem enter the exchanger not at 1700° but at 1400°F . Obviously, one wishes to construct a diagram corresponding to Fig. 3-2 in which the hot-gas curve starts at 1400° instead of 1700°F . This has been done in Fig. 3-3, first reproducing on this latter diagram the hot-gas curve of Fig. 3-2 as a

dotted line. Now the temperature-heat-content relation of the gas in the new exchanger must be identical with that in the old below the 1400° level. This is equivalent to saying that the curve starting at 1400°F is merely the dotted curve moved to the left parallel to itself.¹ Graphically, this is easily done with dividers.

By fitting the data on specific heats with empirical equations relating the specific heats to temperature, one can develop the relations between heat quantities, temperature, and temperature differences by purely analytical methods, if one prefers. In the present case, in which the heat capacities of the two streams are relatively insensitive to temperature, approximate results can be obtained very simply by assuming that the specific heat of each stream is constant over the range of temperatures involved. If t' equals the outlet temperature in the limiting case when $T_2 = t_2$ and the specific heats of the air and hot exit gases are assumed to be 7.0 and 7.5, respectively, then by an energy balance around the exchanger $7.0(0.87)(t' - 60) = 7.5(1700 - t')$. Solving, $t' = 964^{\circ}\text{F}$. This value agrees reasonably well with that of 990°F obtained by the more accurate method of Fig. 3-2. In general, an algebraic method is best suited for approximate calculations when specific heats are almost constant or vary nearly linearly with temperature, so that the average specific heat of each substance may be taken as equal to its instantaneous specific heat at the temperature halfway between the initial and final temperature. In more complicated situations, or where a fairly high degree of accuracy is desired, graphical methods are usually shorter and, because they aid in visualization of the problem, less subject to error.

Countercurrent heat exchange. While parallel flow is desirable in certain instances, it has the serious disadvantage that only a relatively low percentage of the heat in the hot stream can be recovered before further removal is blocked by the limitations of thermal equilibrium. A more common practice, therefore, is to make use of countercurrent operation.

Illustration 2. A furnace is fired with a natural gas that is substantially pure CH_4 . The fuel is burned with 20% excess air, and combustion is practically complete. The flue gases leave the furnace at 1500°F , and it is desired to install a countercurrent exchanger in which the heat in the flue gases will be used to preheat the air supply to the furnace, thus reducing the consumption of fuel. In order to avoid any possible complications due to cracking, which may plug flues with deposited carbon, no attempt will be made to preheat the fuel. The average temperature of the air supply may be taken as 60°F . What are the temperature and heat-transfer relationships in an exchanger of this type?

¹ For the mathematical significance of this relation, see p. 70.

Discussion. A diagram of the setup is given in Fig. 3-4.

Choose 10 lb mols of CH_4 as a basis. According to the reaction $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$, 10 mols of CO_2 and 20 mols of H_2O are produced by combustion. The excess O_2 is $20(0.20) = 4$ mols. The N_2 in the air, which equals the N_2 in the flue gas, is $20(1.20)(79/21) = 90$ mols. The O_2 in the air is $20 + 4 = 24$ mols. Thus, on a basis of 10 mols of CH_4 , the material balance is completely established.

Application of an energy balance to the case of countercurrent heat exchange is not quite so straightforward as in parallel flow. If one decides to work with Q , the heat transferred from the gas to the air between the hot end of the exchanger and an intermediate section, represented by the dotted line in the diagram, it is easy enough to find the relationship between Q and T , by the method employed in Illustration 1.

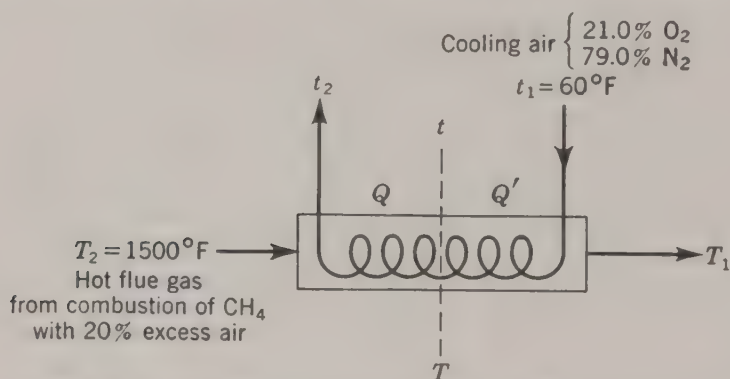


FIG. 3-4. Countercurrent heat exchanger of Illustration 2.

However, it is impossible to make a direct calculation of the relation between Q and t , because in the case of countercurrent heat exchange both t and t_2 are unknowns. If, on the other hand, one tries to work with Q' , defined as the heat transferred from the gas to the air between the dotted line and the cold end of the exchanger, the preceding situation is reversed. It is then easy enough to find the relation between Q' and t , but the relation between Q' and T cannot be computed directly, since both T and T_1 are unknown.

In principle, the solution is to assume a series of values for the exit temperature of either the gas or the air. For each value assumed, the relation between t , T , and the heat transferred in that portion of the exchanger between the intermediate section and the end of the exchanger where conditions are fixed can be computed.

As in the preceding illustration, calculations are simplified if one will first prepare a plot of the temperature of each stream against its sensible-heat content. In the parallel-flow case it was advantageous to calculate the sensible-heat content of the cold-air stream above its inlet tempera-

ture, 60°F, and that of the hot-gas stream below its inlet temperature, 1700°F. The reason for this was that the two streams entered the same end of the exchanger at these two temperatures and that a heat balance required that, up to any point in the exchanger, the changes in sensible-heat contents of the two streams be equal. In the counterflow problem there is no point in the exchanger at which the temperatures of both gas streams are known in advance. Consequently, one does not have a priori a logical basis from which to calculate the changes in sensible heat. The best thing to do is to start by preparing a plot of temperature against the sensible-heat content of each of the two streams, both constructed relative to 60°F. The calculations are arranged in Table 3-3 and presented graphically in Fig. 3-5.

TABLE 3-3. SENSIBLE-HEAT CONTENTS OF HOT GAS AND AIR ABOVE 60°F
(ILLUSTRATION 2)

A	Temperature, °F.....	300	600	900	1200	1500
B	A - 60.....	240	540	840	1140	1440
C	$Mc_{p,av}^{\circ}$ at A: CO ₂	9.4	10.1	10.7	11.2	11.5
D	O ₂	7.1	7.3	7.5	7.7	7.8
E	N ₂	7.0	7.0	7.1	7.3	7.4
F	H ₂ O.....	8.1	8.3	8.5	8.7	9.0
G	10(C)(B).....	23,000	55,000	90,000	128,000	166,000
H	4(D)(B).....	7,000	16,000	25,000	35,000	45,000
I	90(E)(B).....	151,000	340,000	536,000	750,000	960,000
J	20(F)(B).....	39,000	90,000	143,000	199,000	259,000
K	G + H + I + J = sens.-heat content of gas, Btu.....	220,000	501,000	794,000	1,112,000	1,430,000
L	24(D)(B).....	41,000	95,000	151,000	211,000	270,000
M	I + L = sens.-heat content of air, Btu.....	192,000	435,000	687,000	961,000	1,230,000

The next step is to assume a value of the outgoing temperature of one of the gas streams, such as T_1 . For example, let $T_1 = 1000^{\circ}\text{F}$. From Fig. 3-5 it is obvious that the heat lost by the hot-gas stream in this exchanger in cooling from 1500°F to 1000°F is $1,430,000 - 905,000 = 525,000$ Btu. Heat balance requires that this heat quantity be also the increase of sensible heat of the air stream. From Fig. 3-5 one sees that this requires that the air rise in temperature to 705°F.

On the basis of the assumption made, the temperatures of both streams at both ends of the exchanger are now known, and the inlet and outlet temperature points may be plotted against the quantity of heat Q' transferred in the exchanger starting from the cold end. The problem is to construct the curves of temperatures T and t , to be plotted against Q' , for the two streams between these limiting values.

For the air temperature t it is clear that the air curve of Fig. 3-5 is the

relation required. For the hot gases, the corresponding curve is the sensible-heat content of those gases measured above 1000°F as a base. This can be calculated by the method used in constructing the curves of Fig. 3-2. The result is the upper curve on Fig. 3-6. Study of the situation will show that this curve is identical with the section of the hot-gas curve of Fig. 3-5 from 1000°F up to 1500°F , plotted against the heat content,

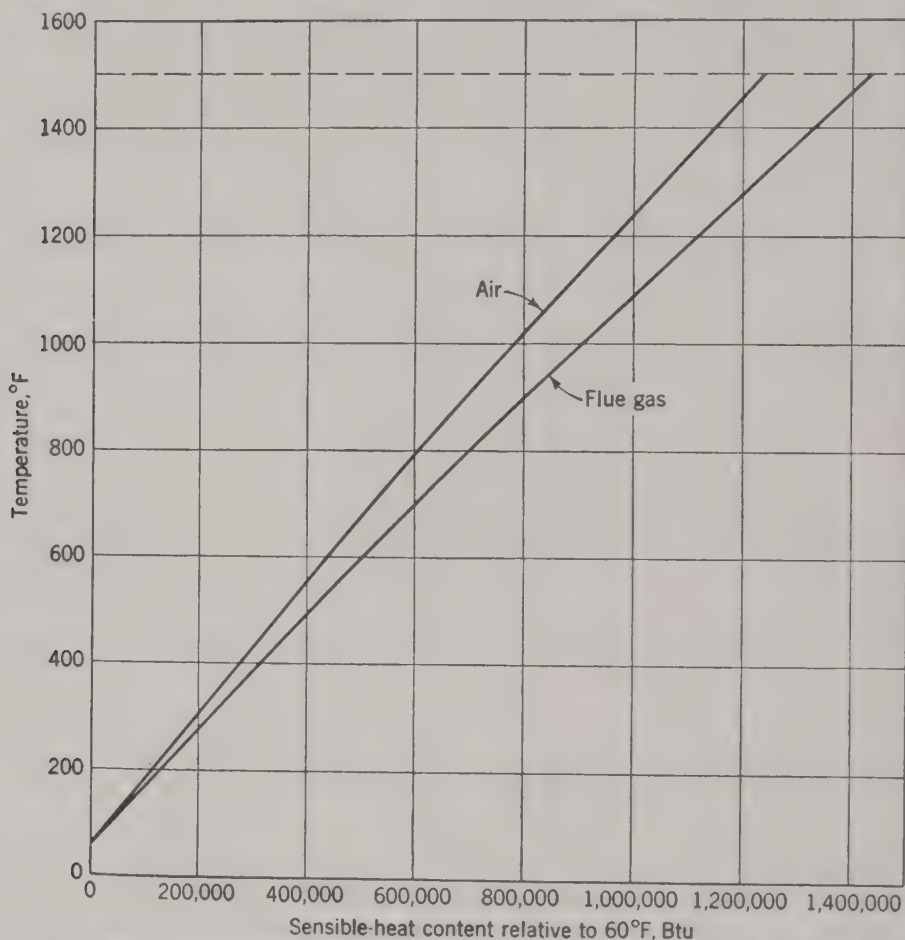


FIG. 3-5. Sensible-heat contents of gas and air streams in countercurrent heat exchanger of Illustration 2.

not above 60°F as in Fig. 3-5, but above 1000°F . This in turn is equivalent to moving the hot gas curve of Fig. 3-5 horizontally from right to left, all points of the curve traveling the same distance to the left.

The corresponding result for the case in which $T_1 = 500^{\circ}\text{F}$, secured by exactly the same type of procedure, is also shown on Fig. 3-6.

It is obvious that Fig. 3-6 is exactly like Fig. 3-5, except that the curve for the flue gas has been shifted horizontally. The extent of the shift is governed by the assumption made as to the value of T_1 . As in Illus-

tration 1, it can be assumed that the coefficient of heat transfer in the exchanger is roughly constant and the major variable in the physical setup is the heat-transfer area of the exchanger. If a small exchanger is used, the total amount of heat transferred in the apparatus will be small, the value of T_1 will be high, and the curve for the gas temperature will be shifted relatively far to the left on Fig. 3-6, as, for example, in the case in which $T_1 = 1000^\circ\text{F}$. If a somewhat larger exchanger is installed, the

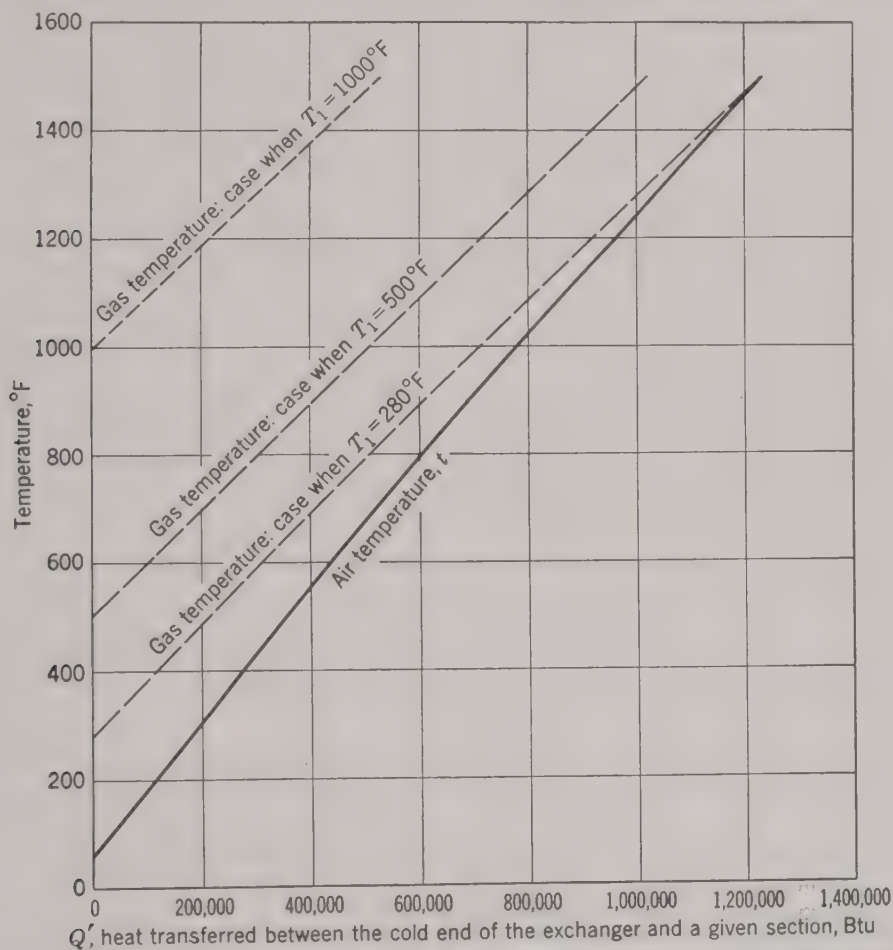


FIG. 3-6. Temperature distribution in countercurrent heat exchanger of Illustration 2.

total amount of heat abstracted from the gas will be greater, the value of T_1 will be lower, and the curve for the gas temperature will be shifted more to the right, as in the case in which $T_1 = 500^\circ\text{F}$.

As the curve for the gas temperature is shifted progressively to the right, it is clear that the temperature difference between the gas and the air at any given section of the exchanger becomes smaller and smaller; eventually, as the curve is shifted still farther to the right, a condition must be reached in which a zero temperature difference exists at some

point in the exchanger. On the diagram, a zero temperature difference corresponds to an intersection of the curves for gas and air. However, since the temperatures in the apparatus cannot exceed 1500°F or drop below 60°F , one need consider no intersections that may occur outside these temperature limits. Focusing on the possibility that the curves intersect in the range between 1500°F and 60°F , one sees that, as the gas curve is shifted horizontally to the right, the first point at which an intersection can occur is at 1500°F , *i.e.*, at the hot end of the exchanger. When the curves intersect at 1500°F , the value of Q' read from Fig. 3-6 is 1,230,000 Btu. The sensible-heat content of the gas at T_1 must equal the sensible-heat content of the gas at 1500°F minus Q' , or

$$1,430,000 - 1,230,000 = 200,000 \text{ Btu}$$

From Fig. 3-6, $T_1 = 280^{\circ}\text{F}$, the lowest temperature to which it is possible to cool the flue gas in a heat exchanger under the specified conditions.

In mathematical terminology, the process of shifting the curve for the gas temperature in a horizontal direction on Fig. 3-6 is equivalent to choosing different values for the arbitrary constant of integration that results from integrating a differential equation. Let n represent the number of mols of the gas or air stream. The heat transferred to the air in a differential length of the exchanger equals the differential temperature rise times the number of mols times the corresponding molal heat capacity,

$$dQ' = (nMc_p^{\circ})_{\text{air}} dt$$

The heat given up by the gas in the same element equals

$$dQ = -(nMc_p^{\circ})_{\text{gas}} dT$$

An energy balance on a differential element of the exchanger yields the differential equation

$$(nMc_p^{\circ})_{\text{air}} dt = -(nMc_p^{\circ})_{\text{gas}} dT$$

Integration leads to the result $\int (nMc_p^{\circ})_{\text{air}} dt + \int (nMc_p^{\circ})_{\text{gas}} dT = C$, where C is an arbitrary constant. If heat capacities can be expressed as functions of temperature, the first term on the left-hand side of the integrated energy-balance equation is seen to be a function of the air temperature t only, and the second term a function of the hot-gas temperature T only. The equation is therefore directly integrable, but the arbitrary constant of integration can only be determined provided that a pair of corresponding values of t and T at some specific point in the exchanger is known. Initially, the temperature of the hot gas at the hot end of the exchanger was given (1500°F), but the value of t_2 was unknown. At the cold end, the air temperature t_1 was given (60°F), but the value of T_1 was unknown. However, if one fixes both temperatures at either end of the unit or at any intermediate point, *e.g.*, by fixing T_1 in the hot exit gas as discussed, one can solve the integrated equation for the arbitrary constant C . Once the value of C is known, the relation between t and T is established.

In handling the data of the problem, advantage was taken of the fact that the right-hand term in the expression for dQ' is a function of t only, and in the expression for dQ it is a function of T only. This enables one to integrate these two expressions and plot each temperature, independently of the other, against the corresponding integrated changes in heat content of the two streams.

Inasmuch as the curves for various gas temperatures are all parallel, the labor of obtaining the curve for the limiting case can be greatly reduced by preparing a graph of the sensible-heat content of the two streams above any convenient base and then using dividers to lay off parallel curves.

In Illustration 1, the "bottleneck" due to thermal equilibrium was approached at the cold end of the exchanger, and in Illustration 2 it has been shown that the "bottleneck" is at the hot end of the exchanger, but it is not safe to generalize and assume that as the area of an exchanger is increased the approach to thermal equilibrium will always take place at one end or the other of the apparatus. For example, a change in the relative amounts of the hot and cold streams may shift the "bottleneck" from one end of an exchanger to the other. Where the enthalpy (or heat-content) curves for the individual streams have low curvature, study of the diagrams will make it clear that the bottleneck or pinch point of minimum temperature difference always tends to occur at that end of the exchanger which is the point of entrance of the stream of higher heat capacity.

If sensible-heat effects are not the only ones involved and one or both of the streams undergo change of phase during their passage through an exchanger, the situation is handled as described above, except that the values of heat content must include not only sensible heat but also latent heats, heats of chemical reactions, etc. When this is done, the curves of a plot analogous to Fig. 3-6 may show plateaus or breaks. The possibility exists that, when one curve is shifted horizontally, the point at which it first touches the other curve may lie somewhere in the middle of the exchanger, rather than at one end. A case of this sort is encountered in the next problem.

Illustration 3. A small chemical manufacturer is located in a region where the only readily available fuel is a sweet (low H_2S), lean (practically pure CH_4), natural gas, which, however, is expensive. A long-term contract for purchase of the gas is due to expire in the near future, and the general economic situation is such that the new contract to be negotiated will undoubtedly call for an appreciable increase in price. Hence, the manufacturer is exploring possibilities for further economy of fuel in his operations.

At present, heat is recovered from the flue gases in the manufacturer's plant by means of a waste-heat boiler. On a basis of 10 lb mols of CH_4 burned with 20% excess air, the flue gases contain 10 mols of CO_2 , 4 mols of O_2 , 90 mols of N_2 , and 20 mols of H_2O , or a total of 124 mols. In this particular plant, a considerable fraction of the feedwater to the boilers is condensate from process steam. This condensate is employed in a feed-water heater to bring the hot combustion gases down to 240°F . How-

ever, in addition to this condensate, for each 10 lb mols of CH_4 burnt, there are 2000 lb of fresh, cold make-up feedwater at an average temperature of 48°F .

Normally, it is not economical to recover heat from flue gases at temperatures below 240°F , because of low rates of heat transfer and corrosion difficulties; but in this particular situation it may be worth considering, and the manufacturer wishes to make a preliminary study of the possibility. In a countercurrent heat exchanger, what is the lowest temperature to which the flue gases leaving the waste-heat boiler can be cooled, by using them to heat the cold make-up feedwater?

Solution. As in the preceding example, the first step is to construct a plot of temperature vs. enthalpy for each of the two streams passing through the exchanger (Fig. 3-7). Since the lowest temperature in the

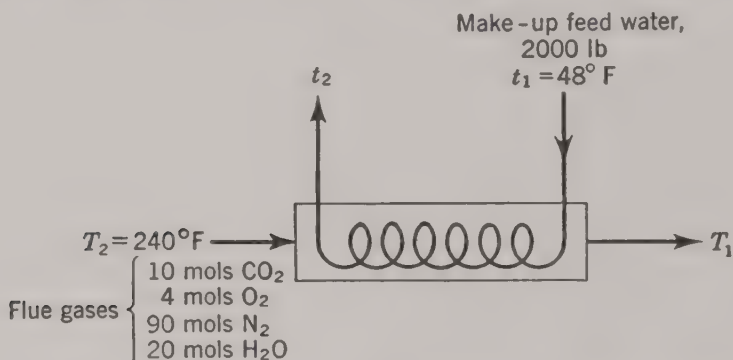


FIG. 3-7. Countercurrent heat exchanger of Illustration 3.

apparatus is 48°F , it is convenient to let the enthalpies of gaseous CO_2 , O_2 , and N_2 and liquid H_2O be zero at 48°F .

It is sufficiently accurate for engineering purposes to consider that the specific heat of liquid water in the range involved has a constant value of unity. Hence, at any temperature t in degrees Fahrenheit, the heat content of the feedwater in Btu above 48° is $2000(t - 48)$. The heat content is linear in t , and a plot of the curve for the feedwater vs. t is the solid straight line shown on Fig. 3-8.

In calculating the heat content of the flue-gas stream, it is necessary to remember that condensation of water vapor will take place at temperatures below the dew point of the gas. This condensate tends toward both thermal and partial-pressure equilibrium with the gas, even though complete equilibrium may not be achieved. If normal barometer is assumed, the partial pressure of water vapor in the gases leaving the waste-heat boiler equals $29.9(20/124) = 4.82$ in.Hg. Reference to the steam tables¹

¹ J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York, 1936. Steam tables in condensed form are given in Table A-4 in the Appendix.

or to vapor-pressure tables shows that pure water has a vapor pressure of 4.82 in. Hg at a temperature of 132.4°F. Accordingly, no condensation occurs so long as the gas temperature remains above this point, but as the gas is cooled below 132.4°F, increasing amounts of water condense. At any given temperature, the amount condensed is determined by the fact that gas and liquid will be in equilibrium, *i.e.*, the partial pressure of water vapor in the gas will equal the vapor pressure of liquid water at the same temperature.

The technique of computation can be shown by a sample calculation for a flue-gas temperature of 104°F. The vapor pressure of water at this temperature is 2.18 in. Hg. Hence, the partial pressure of the dry gas,

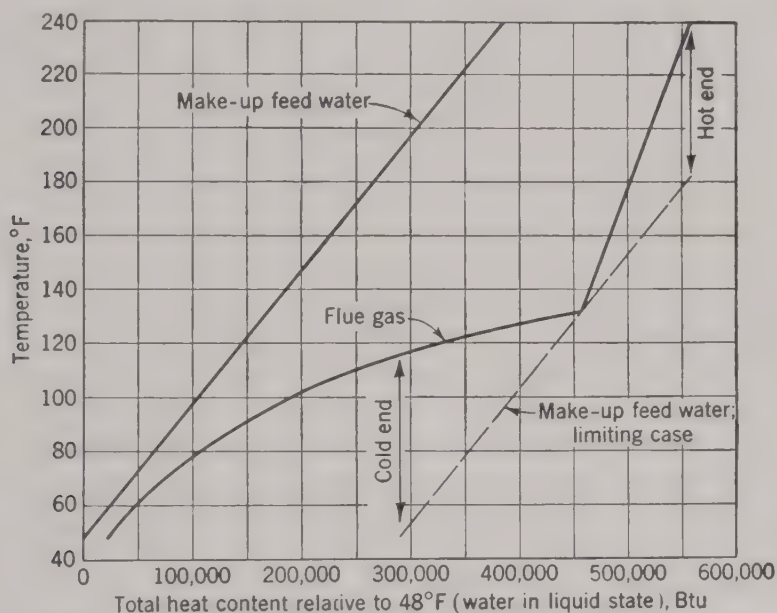


FIG. 3-8. Total heat content of the flue gas and feedwater in the heat exchanger of Illustration 3.

104 mols in amount, is $29.92 - 2.18 = 27.74$ in. Hg. The number of mols of water vapor left uncondensed is $104(2.18/27.74) = 8.2$. By difference, the water condensed is $20 - 8.2 = 11.8$ mols.

For the make-up feedwater stream, zero heat content or enthalpy has already been taken as that of liquid water at 48°F. The same temperature is taken as base for the gas stream, but the water vapor in that stream is condensable. It does in fact condense in the process and gives up heat in doing so. Consequently, it is desirable (although not essential) to call the zero of enthalpy of the water component of the gas stream that of liquid water at 48°F. For the other components, the zero of enthalpy is that of the material as gas at 48°F.

For the water, computation is greatly simplified by the fact that the steam tables give its enthalpies directly at the various conditions involved.

The following calculation gives the heat content of the gas at 104°F:

	<i>Btu</i>
Sensible heat of liquid water, 11.8(18)(72 - 16).....	11,900
Enthalpy of water vapor, 8.2(18)(1107 - 16).....	161,000
Sensible heat of CO ₂ ,* 10(8.9)(56).....	5,000
Sensible heat of O ₂ , 4(7.0)(56).....	1,600
Sensible heat of N ₂ , 90(7.0)(56).....	35,300
Total heat content of flue gases at 104°.....	214,800

* Average values of $M\bar{c}_p^\circ$ for the various gases may be taken from Fig. 1-3, since the differences between average values based on a datum of 60°F and those based on 48°F are not large enough to affect the results significantly.

If steam tables had not been available, the enthalpy of water vapor could have been calculated in accordance with the principles developed in physical chemistry, by computing the changes in enthalpy for any convenient series of steps the net result of which is the conversion of liquid water at 48°F and the corresponding vapor pressure to water vapor at 104°F and a partial pressure of 2.18 in. Hg. For example, one might vaporize the water at 48°F and 0.34 in. Hg (the vapor pressure), heat the resulting vapor from 48°F to 104°F at constant pressure, and then compress the vapor at constant temperature from 0.34 in. Hg to 2.18 in. Hg. The enthalpy change for the first step is the heat of vaporization at 48°F, 1067 Btu/lb. The enthalpy change for the second step, as obtained from Fig. 1-3, is $8.0(104 - 48)/18 = 25$ Btu/lb. Since the enthalpy of a perfect gas is a function of temperature only and is independent of pressure, and since the perfect-gas laws are closely approximated by water vapor at the temperatures and pressures in question, the enthalpy change for the third step may be considered as negligible. The net enthalpy change for the three steps is therefore $1067 + 25 = 1092$ Btu/lb. The comparable figure obtained from the steam tables, as shown in the calculations above, is $1107 - 16$, or 1091 Btu/lb.

The total heat content of the flue gases has been calculated at a number of different temperatures and the results plotted in Fig. 3-8, together with the line for the cold feedwater.

As in Illustration 2, a representation of the various possible temperature distributions in a countercurrent heat exchanger may be obtained by shifting either curve in a horizontal direction. In this example, it is easier to move the curve for the cold water, since it is a straight line. The limiting case occurs when the water line is shifted far enough to the right so that it is to the right of the flue-gas curve at all points in the exchanger, except one at which it just touches. The line is shown dotted on Fig. 3-8. It is obvious that the bottleneck in this exchanger is in the middle of the apparatus, not at either end. The diagram also shows that the flue-gas temperature at the cold end of the exchanger in the limiting case is

116°F. In any actual exchanger, operating with a finite temperature difference between gas and water at all points, the water line will lie somewhere to the right of the dotted line, and the temperature to which the flue gas is cooled will be greater than 116°F.

The preceding illustrations have involved heat effects corresponding to physical changes only. It is now necessary to take up in addition the heat effects resulting from chemical reaction.

COMPLETE COMBUSTION

The energy balance on a combustion operation involves an accounting of the input and output of five forms of energy: chemical energy (the heat of combustion), the latent heat of vaporization of water vapor in entering and leaving streams, sensible heat in entering and leaving streams, heat losses through the walls, and useful heat delivered to the heat sink¹ in the process. As a datum temperature, it is conventional to choose that of the ambient air and assign a value of zero to the heat content of gaseous O_2 , N_2 , CO_2 , and SO_2 and liquid water at this temperature. An equally valid practice is to let the enthalpy of water be zero for water vapor at the ambient air temperature and a pressure equal to the vapor pressure of water at this temperature. Normally, the results of material-balance calculations on the combustion operation itself can be applied only to determining the first three items in the energy balance listed above, and the sum of the other two items is obtained by difference.

Heats of combustion. The heats of combustion of some of the more important compounds found as components of fuels are given in Table 3-4.

Heats of combustion change with temperature but the differences between the values listed in the table and those in the normal atmospheric temperature range are small and ordinarily neglected. The difference between the higher and lower heating values of hydrogen, 10,519.7 cal/g mol, is the latent heat of vaporization of water at 25°C. As in the case of heats of combustion, the value of latent heat thus derived from the table is usually employed without correction, even though the temperature chosen as datum may differ by quite a few degrees from 25°C.

¹ The term "heat sink" refers to the material at lower temperature that is the acceptor of heat in a heat-transfer process. Usually, though not necessarily, the quantity of material comprising the sink is indefinitely large so that the acceptance by it of a finite quantity of heat does not change its temperature. The water in a river or in a spray pond or the surrounding air are examples of heat sinks for accepting waste heat from a process. As used in the text above in the sense of accepting useful heat, the term "heat sink" refers to the "charge" of a batch process or to the "feed" of a continuous process. Thus, it might be the feedwater to a boiler or the crude-oil feed to the coils in the furnace of a petroleum still.

In the usual calorimetric techniques for determining the heating value of a fuel, water is condensed. Hence, unless otherwise specified, it can be taken for granted that a reported figure is the higher heating value.

An illustration of the use of heats of combustion and sensible heats is the determination of the portion of the heat released in combustion of a fuel which can be delivered to a process requiring heat input at a high temperature level. This problem of the temperature level at which heat is available for effective use is associated with the question of heat recovery, discussed in the preceding section. Both problems rise from the fact

TABLE 3-4. MOLAL HEATS OF COMBUSTION AT CONSTANT PRESSURE
In gram calories per gram mol = Chu per pound mol

Fuel	Higher heating value, water condensed	Lower heating value, water uncondensed	Ref.	Temp., °C
Carbon (amorphous C to CO ₂).....	97,000	97,000	1	25
Hydrogen (H ₂).....	68,318.1	57,798.4	2	25
Carbon monoxide (CO).....	67,636.1	67,636.1	2	25
Methane (CH ₄).....	212,950	191,910	3	18
Ethane (C ₂ H ₆).....	373,050	341,500	3	18
Ethylene (C ₂ H ₄).....	336,600	315,600	3	18
Acetylene (C ₂ H ₂).....	311,100	300,600	3	18
Propane (C ₃ H ₈).....	526,300	484,200	4	18-20
Propylene (C ₃ H ₆).....	490,200	458,700	4	18-20
Benzene (liq. C ₆ H ₆).....	787,200	755,700	4	18-20
Sulfur (rhombic S to SO ₂).....	70,920	70,920	3	18

1. The heating value of amorphous carbon varies somewhat with the source and history. The value given is an approximate average.

2. F. D. Rossini, *J. Res. NBS*, **22**, 407 (1939).

3. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

4. International Critical Tables, Vol. V, p. 162, McGraw-Hill Book Company, Inc., New York, 1929.

that in many chemical furnaces a considerable portion of the heat must be supplied at a high temperature, whereas in ordinary power-plant boiler furnaces the heat can all be absorbed at relatively low temperatures.

Illustration 4. Consider the combustion of a producer gas containing 4.8% CO₂, 27.0% CO, 0.4% O₂, 1.9% CH₄, 14.1% H₂, and 51.8% N₂, with 50% excess air. Gas and air enter the combustion chamber dry at 60°F. It is desired to employ the products of combustion as the source of heat for a furnace requiring the input of heat at temperatures of 2000°F and above. If heat losses from the combustion chamber and furnace to the surroundings are negligible and the products of combustion

are cooled to 2000°F before they leave the furnace, what percentage of the lower heating value of the fuel is delivered to the furnace?

Solution. A diagram of the process is given in Fig. 3-9.

On the basis of 100 mols of producer gas, the combustion products are 33.7 mols CO₂, 12.0 O₂, 186.8 N₂, and 17.9 H₂O, totaling 250.4 mols.

Let the datum temperature be 60°F, with zero enthalpy assigned to water in the vapor state. Thus, sensible heat in all entering streams is zero. This method of accounting eliminates latent heat of water as an

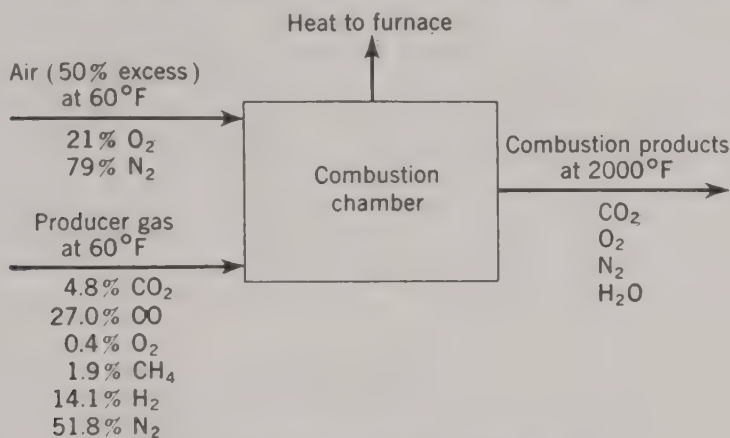


FIG. 3-9. Combustion chamber of Illustration 4.

item. The total input, then, is the lower heating value of the fuel. In view of the fact that a high degree of precision in the calculations is not justified for most engineering applications, only three significant figures will be carried in the heating values employed.

<i>Input</i>	<i>Btu</i>
CO: 27.0(67,600)(1.8).....	3,290,000
CH ₄ : 1.9(192,000)(1.8).....	660,000
H ₂ : 14.1(57,800)(1.8).....	1,470,000
Total.....	5,420,000

The total input must equal the heat utilized in the furnace plus the sensible heat in the products of combustion from it. The latter is obtained by the methods of the preceding section, using heat capacities from Fig. 1-3. Thus

$$[33.7(12.1) + 12.0(8.0) + 186.8(7.6) + 17.9(9.4)](1940) = 4,060,000 \text{ Btu}$$

By difference, the heat delivered to the furnace is

$$5,420,000 - 4,060,000 = 1,360,000 \text{ Btu}$$

Expressed as a percentage, the result is

$$1,360,000(100)/5,420,000 = 25.1\%$$

of the lower heating value that is delivered to the furnace. The low magnitude of the answer emphasizes the importance of heat recovery.

This analysis, which shows that only a quarter of the chemical heat of combustion is available at 2000°F, should make it completely clear that, in the absence of preheat, the percentage of the heat available will decrease progressively as the furnace temperature goes up and will disappear at some specific temperature level. This temperature is the so-called theoretical flame temperature (although sometimes this term is restricted to combustion with theoretical air). It should be equally clear that the heat available at any specific temperature level of the furnace can be increased by supplying heat to air or fuel by any suitable method of preheating them and, furthermore, that by such preheating it is possible to get heat available in the furnace at temperature levels that may be far above the theoretical flame temperature as above defined. Using a given fuel and an agreed-upon air supply, one can calculate directly the net heat available at any specified furnace-temperature level. A graph of the result gives the engineer the clearest picture of the thermal potentialities of such a combustion process.

Illustration 5. The producer gas of Illustration 4 is burnt as described, using 50% excess air and with both fuel and air supplied at 60°F. Plot the percentage of the heat of combustion of the fuel available against the temperature level at which the gaseous products of combustion leave the furnace itself.

Solution. From Illustration 4, the heat input is 5,420,000 Btu per 100 mols of fuel. The sensible-heat content of the furnace gases is computed in Table 3-5 (line K), and the net heat available obtained by difference (line L).

TABLE 3-5. COMPUTATION OF HEAT AVAILABLE FROM COMBUSTION OF PRODUCER GAS

A	Assumed temperature, °F.....	2000	2540	2760	3150	3500*
B	A - 60.....	1940	2480	2700	3090	3440
C	$M_{c,av}^{\circ} N_2$	7.6	7.7	7.8	7.9	8.0
D	O ₂	8.0	8.1	8.2	8.3	8.4
E	H ₂ O.....	9.4	9.7	9.9	10.2	10.5
F	CO ₂	12.1	12.5	12.6	12.9	13.0
G	186.8 (B)(C).....	2,750,000	3,560,000	3,920,000	4,550,000	5,135,000
H	12 (B)(D).....	186,000	241,000	265,000	308,000	347,000
I	17.9 (B)(E).....	326,000	430,000	478,000	560,000	646,000
J	33.7 (B)(F).....	792,000	1,045,000	1,145,000	1,340,000	1,508,000
K	G + H + I + J.....	4,054,000	5,276,000	5,808,000	6,768,000	7,636,000
L	5,420,000 - K.....	1,366,000	144,000	-388,000	-1,338,000	-2,216,000
M	(L/5,420,000)100....	25.1	2.6	-7.1	-24.7	-40.9

* Computations in this column neglect dissociation of CO₂ and H₂O.

From Fig. 3-10 it is seen that the percentage of the heat of combustion available for use becomes zero at 2600°F. Consequently, that is the theoretical flame temperature.

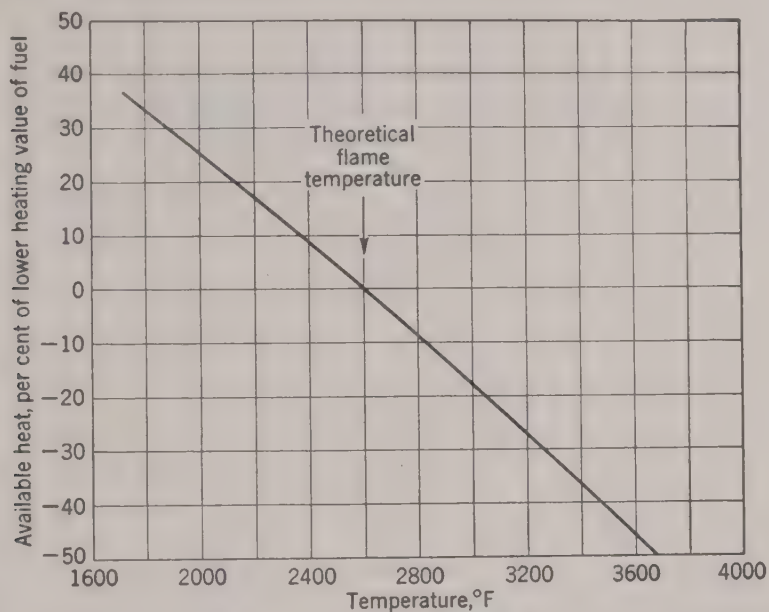


FIG. 3-10. Relation between the temperature at which the products of combustion leave the combustion chamber of Illustration 5 and the heat available for process requirements.

It frequently is necessary in a process to have a furnace temperature that is higher than the theoretical flame temperature of the fuel which is available. In most cases this temperature is obtained by the use of preheat.

Illustration 6. The same producer gas employed in Illustration 4, entering under the same conditions and with 50% excess air, as before, is to be used in a furnace equipped with a combustion chamber which is substantially adiabatic. The gases from the combustion chamber are discharged into a heat-absorbing section of the furnace and flow in this section countercurrent to the furnace charge. It is essential that the gases enter this section from the combustion chamber at 3500°F. To what temperature is it necessary to preheat air and fuel to permit attainment of the desired temperature? In this particular instance, the purpose for which the answer is to be used requires only an approximate value, and therefore it is agreed to neglect any effects due to dissociation of the products of combustion, although the effects are not entirely negligible at 3500°F.

Solution. In Illustration 5, the heat content of the combustion gases at 3500°F was calculated to be 2,216,000 Btu more than the heat of combustion. Consequently, for this problem it is necessary only to compute

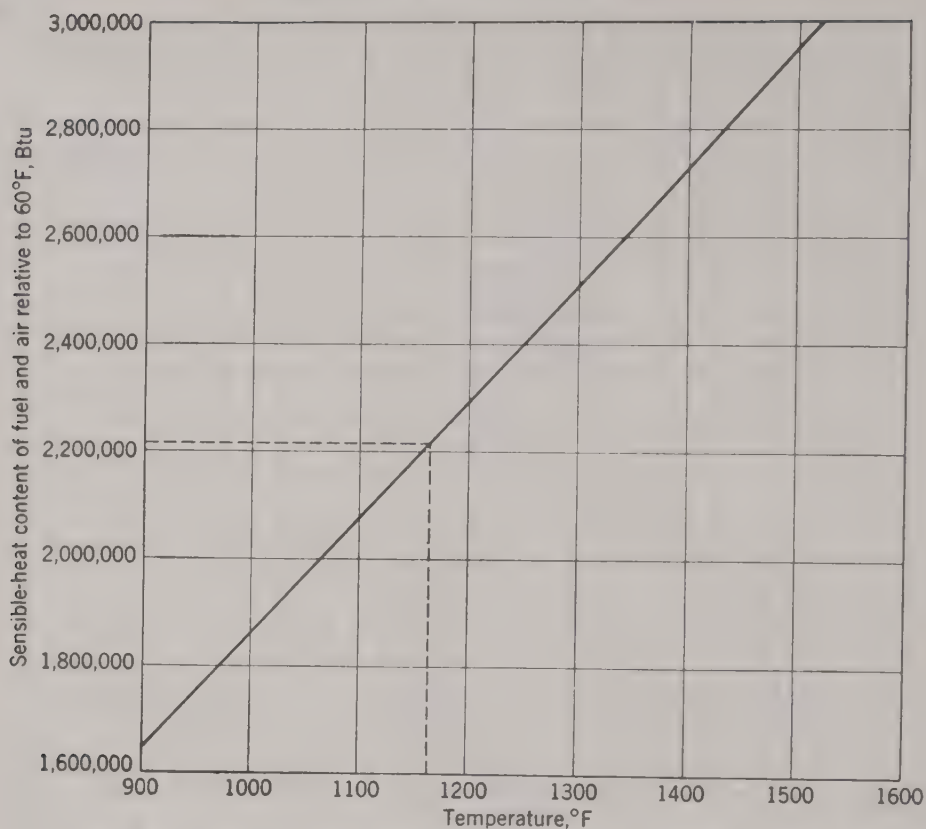


FIG. 3-11. Determination of the preheat temperature in Illustration 6.

the temperature at which 100 mols of producer gas plus the equivalent amount of air will contain that amount of sensible heat. On a basis of 100 mols of producer gas, the amount of air equivalent to a 50% excess is $3(12)(100/21) = 171$ mols. Of this, 36 are oxygen and 135 are nitrogen. The simplest method of solution is to make a plot of heat content

TABLE 3-6. CALCULATION OF HEAT CONTENT OF FUEL PLUS AIR AT VARIOUS PREHEAT TEMPERATURES

Gas	Mols	$Mc^{\circ}_{p,av}$ up to				Sensible heat at			
		900°	1100°	1300°	1500°	900°	1100°	1300°	1500°
CO ₂	4.8	10.7	11.0	11.3	11.5	43,200	55,000	67,000	79,500
CO.....	27.0	7.2	7.3	7.4	7.5	163,000	205,000	248,000	292,000
O ₂	36.4	7.5	7.6	7.7	7.8	229,000	289,000	348,000	409,000
CH ₄	1.9	11.4	12.2	12.9	13.5	18,200	24,100	30,400	37,000
H ₂	14.1	7.0	7.0	7.0	7.1	83,000	103,000	123,000	144,000
N ₂	186.8	7.1	7.2	7.3	7.4	1,112,000	1,400,000	1,690,000	1,990,000
Total....	271.0	1,648,400	2,076,100	2,506,500	2,951,500

vs. temperature as in Fig. 3-11, which is based on the calculations of Table 3-6.

From Fig. 3-11 the temperature to which the gases must be preheated is 1160°F.

Illustration 7. A plant is to be built for “activating” charcoal to convert it to a form having high adsorptive powers. The activation is achieved by contacting the charcoal with steam at 1600°F. It is impracticable to obtain such a high temperature in the usual type of boiler with superheater, because superheater tubes will not stand temperatures much in excess of 800 to 1000°F. Consequently, it is proposed to use for activation a steam-rich mixture of gases at 1600°F, obtained by injecting steam from a boiler into hot flue gases. The steam available is at 150 psig, superheated to 620°F.

The flue gases will be produced by combustion of a fuel oil with a gross heating value of 18,800 Btu/lb and a composition represented by the empirical formula $\text{CH}_{1.6}$. Since it is undesirable to have any free oxygen in the activating gases, the fuel will be burnt with a slight deficiency of air, but for preliminary calculations it may be assumed that theoretical air is used and that the combustion to carbon dioxide and water is complete. The activating gases will be formed by cooling the products of combustion from the flame temperature down to 1600°F by addition of superheated steam. Boiler steam is throttled through a pressure-reducing valve and is injected into the flue gases at atmospheric pressure. Heat losses to the surroundings from the combustion chamber and associated ducts and piping are relatively small and, in this instance, may be neglected. Air and fuel are supplied at an average temperature of 75°F. What will be the composition of the activating gases?

Solution. Let the basis of computation be 100 lb of fuel oil. The carbon burnt is $100/[12 + (1.6)(1.008)] = 7.34$ atoms. The hydrogen in the fuel is $7.34(1.6) = 11.74$ atoms. The theoretical O_2 is

$$7.34 + (11.74/4) = 10.28 \text{ mols}$$

and the corresponding N_2 in the air is $10.28(79/21) = 38.6$ mols. The combustion products, then, are 7.34 mols of CO_2 , 5.87 mols of H_2O , and 38.6 mols of N_2 . Let n = the mols of superheated steam injected into the combustion products.

The energy balance on the operation can be visualized with the aid of Fig. 3-12.

While the choice of a basis for heat content is arbitrary, it is obviously convenient to assign a value of zero enthalpy to gaseous CO_2 , O_2 , and N_2 and liquid water at 75°F. On this basis, the heat content of the entering air is zero, and that of the fuel is 1,880,000 Btu. From the steam tables,

the enthalpy of the steam used is $(1335 - 43)$ Btu/lb, or

$$18(1292) = 23,250 \text{ Btu/mol}$$

Its total heat content is therefore $23,250n$.

Alternatively, this can be determined by using the specific-heat method if one has the additional fact that, in expanding through the reducing valve to atmospheric pressure, the steam drops in temperature to 600°F , where its enthalpy is the same as it was before the valve. Starting with liquid water at 75°F the heat of vaporization is 1051 Btu/lb, or

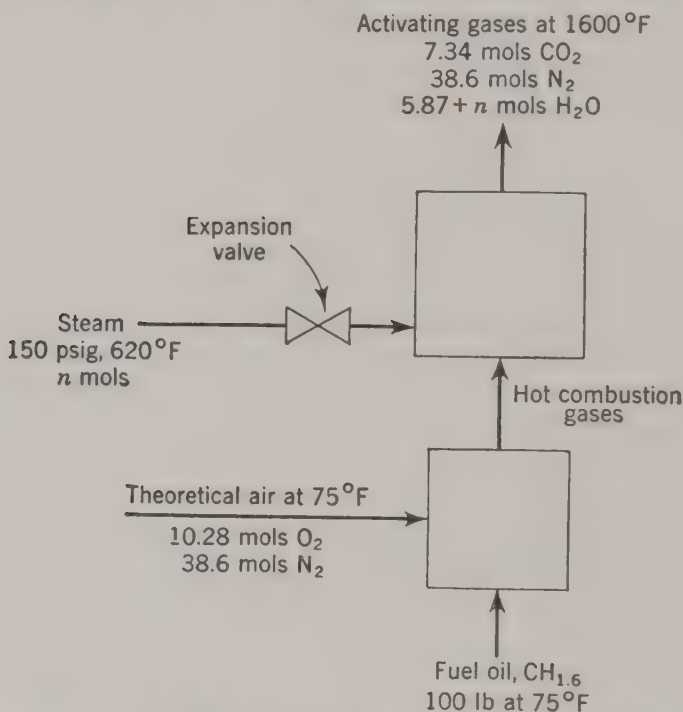


FIG. 3-12. Flow sheet of Illustration 7. Basis: 100 lb of fuel oil.

18,920 Btu/mol, at that temperature. To this must be added the sensible heat needed to raise the steam to 600°F . From Fig. 1-3, the value of $M\bar{c}_{p,av}$ for steam at 600°F is 8.3, giving

$$8.3(600 - 75) = 4360 \text{ Btu/mol}$$

The total heat content of the n mols of added steam is therefore

$$(4,360 + 18,920)n = 23,280n \text{ Btu}$$

The sensible heat of the activating gases is

$$[7.34(11.7) + 38.6(7.4) + 5.87(9.1) + 9.1n](1600 - 75) = (646,000 + 13,900n) \text{ Btu}$$

The latent heat is $18,920(5.87) + 18,920n = (111,200 + 18,920n)$ Btu. The total heat content is therefore $(757,200 + 32,820n)$ Btu.

Applying an energy balance,

$$1,880,000 + 23,280n = 757,200 + 32,820n$$

Solving, $n = 118.0$ mols. The composition of the activating gases is now readily computed as follows:

Basis: 100 lb fuel oil.

Gas	Mols	Per cent
CO ₂	7.34	4.3
N ₂	38.6	22.7
H ₂ O.....	123.87	73.0
Total.....	169.81	100.0

The conclusion drawn from the calculations is that it should be possible, by the proposed arrangement, to produce an activating gas containing over 70% steam. In actual practice, this will be almost as satisfactory as pure steam, because it happens that the rate of activation, in the range of partial pressures between 0.75 atm and 1 atm, is quite insensitive to the partial pressure of the steam.

Illustration 8. A furnace is to be built to deliver 2,500,000 Btu/hr to the stock passing through it. The unit will be fired with producer gas, burnt with 30% excess air. Gas and air enter dry at 60°F and 1 atm, and stack gases leave at 450°F. The material to be heated is sensitive to high temperatures. To eliminate the possibility of overheating at the hot end of the furnace, the combustion of the fuel and the heating of the stock will be segregated into two separate zones and a sufficient quantity of the stack gases leaving the heating zone will be recycled to the combustion chamber to reduce the temperature of the hot gases entering the heating chamber to 1500°F. The analysis of the fuel averages 6.0% CO₂, 23.5% CO, 15.2% H₂, 3.3% CH₄, and 52.0% N₂. Heat losses from the equipment will be neglected.

Calculate the quantity of gas to be handled by the fan in the recycle line, in cubic feet per minute.

Solution. Choose 100 lb mols of fuel as a basis. By methods previously outlined, it is found that the corresponding lower heating value of the fuel is 5,590,000 Btu and the products of combustion are 32.8 mols of CO₂, 7.8 mols of O₂, 179.0 mols of N₂, and 21.8 mols of H₂O, totaling 241.4 mols.

In attacking a problem involving recycle, usually the most fruitful approach is to draw a circle around the whole operation, leaving all

recycle lines within the circle, and set up material and energy balances covering only what crosses the outside boundaries of the plant. Then, after obtaining as much information as possible from the over-all performance of the unit, one can often secure additional information by making material and energy balances around individual parts of the setup.

Begin with an energy balance around the complete installation, considering the flow of energy in and out across the dotted line in Fig. 3-13.

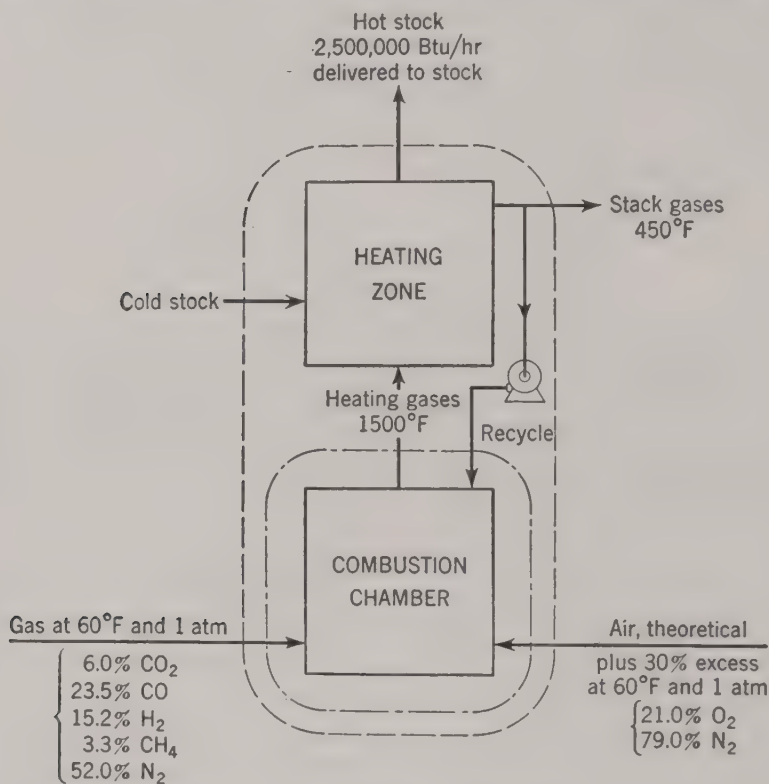


FIG. 3-13. Furnace of Illustration 8.

Assign a value of zero heat content to gaseous CO₂, O₂, N₂, and H₂O at 60°F; and neglect the energy supplied by the fan, which is small compared to the other items in the balance. An energy balance shows that the heat delivered to the stock is the lower heating value of the fuel minus the sensible-heat content of the stack gases at 450°F. The latter, computed by methods already described, amounts to 705,000 Btu, or 2920 Btu per mol. Therefore, on a basis of 100 mols of fuel, the heat to the stock is

$$5,590,000 - 705,000 = 4,885,000 \text{ Btu}$$

The next move is to make a balance around the combustion chamber,¹ letting n = the unknown number of mols of recycled gas.

¹ The heating zone might have been chosen.

The sensible-heat content of the net products of combustion at 1500°F computed in the usual way is found to be

$$[32.8(11.5) + 7.8(7.8) + 179.0(7.4) + 21.8(9.0)](1440) = 2,820,000 \text{ Btu}$$

Since the recycled gas has the same chemical composition as the products of combustion, the sensible-heat content of the recycle at 1500°F is in the same ratio to the sensible-heat content of the products of combustion at 1500°F as the number of mols of recycle is to the number of mols of net combustion products. At 1500°F, then, the heat content of the recycle is $2,820,000(n/241.4) = 11,680n$.

To satisfy an energy balance around the combustion chamber, the energy in the fuel plus that in the air plus that in the recycle at 450°F must equal that in the net products of combustion at 1500°F plus that in the recycle at 1500°F.

$$5,590,000 + 0 + 2,920n = 2,820,000 + 11,680n$$

whence $n = 316$.

With the material and energy balances complete on a basis of 100 mols of fuel, the quantity of gas that must be handled per minute by the recycle fan is

Btu/hr	Mols recycle per hr	Cu ft/min recycled gas at s.c.	
2,500,000	316	359	$\frac{910}{492} = 1790 \text{ cu ft/min of recycled gas}$
	4,885,000	60	

CHEMICAL EQUILIBRIUM

When the primary objective of combustion is not heat but power, as in internal-combustion engines, or intermediate oxidation products, as in producer gas, it is often advantageous to burn fuels with less than the theoretical amount of air. Under these conditions, the combustion reactions may be far from complete. The reactions are also incomplete in high-temperature flames, even in the presence of excess air. In either case, the upper limit on the degree of completion that one can achieve may be the equilibrium composition of the reaction products. If circumstances are such that reaction rate is high, the limit set by equilibrium may be closely approached and the existence of equilibrium can be assumed as a basis of calculation. Where equilibrium is not approached, it is often instructive to determine the degree by which one is failing to approach it, since this offers an important basis for judging the practical potentialities of improving operating conditions.

Data on the equilibrium constants of the combustion reactions are presented in Fig. 3-14. With the exception of the constants for C_2H_4 and

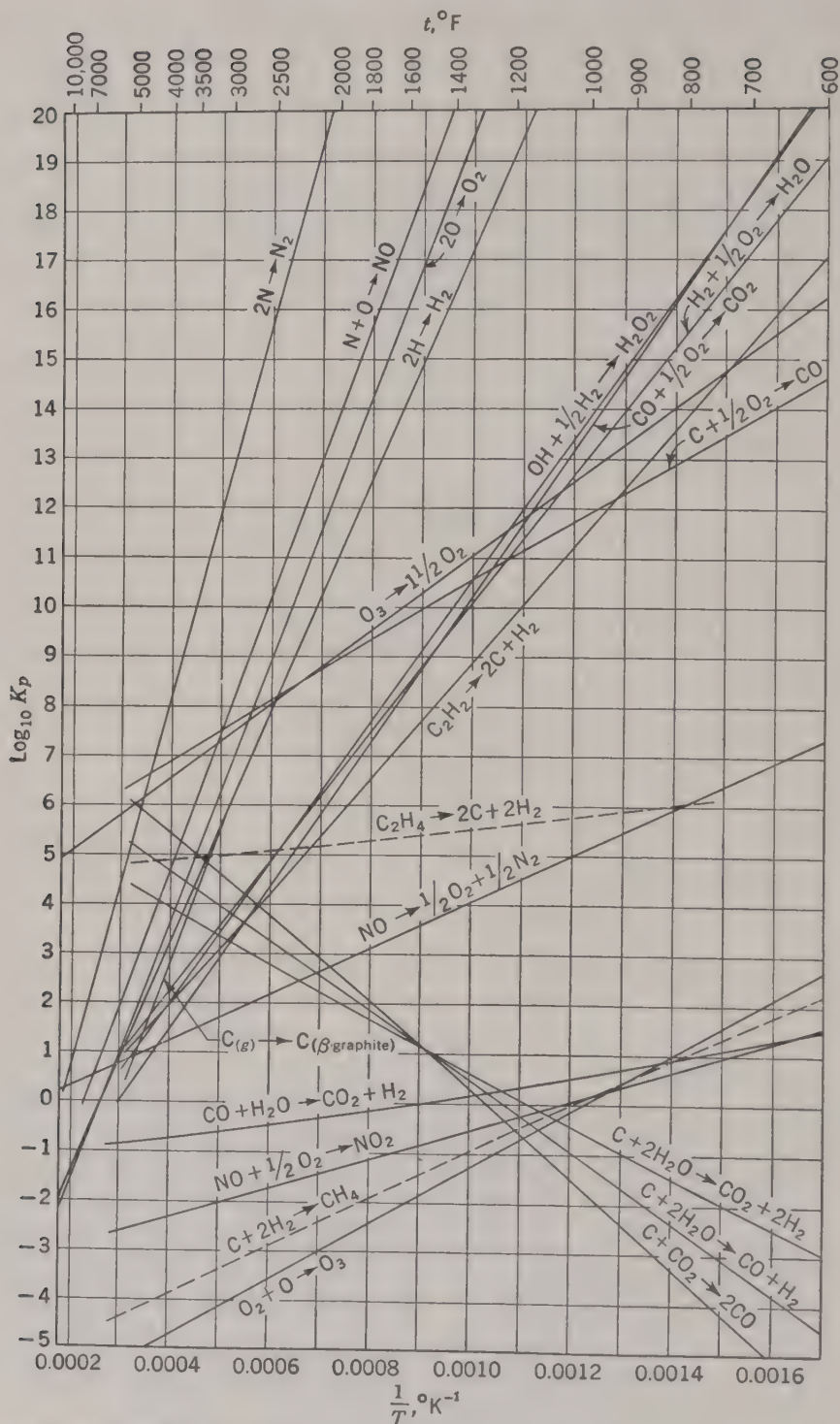


FIG. 3-14. Equilibrium constants of combustion reactions. For the reaction $aA + bB \rightleftharpoons cC + dD$, $K_p = p_C^c p_D^d / p_A^a p_B^b$, with partial pressures expressed in atmospheres. H_2O as vapor; carbon, unless otherwise noted, is β graphite. (This figure is supplied through the courtesy of Professor H. C. Hottel of Massachusetts Institute of Technology.)

C_2H_2 decomposing to carbon and hydrogen, which are taken from Kassel,¹ the values are those recommended by Lewis and von Elbe,² on the basis of a critical survey of the literature.

The illustrations that follow are typical examples of the use of Fig. 3-14 to calculate the composition of a gaseous mixture when the temperature is known. The final illustration involves energy relationships as well as chemical equilibrium.

Formation of NO. The arc process for the fixation of nitrogen depends upon the fact that, when air is heated to high temperature, a certain amount of NO is formed by the reaction $N_2 + O_2 = 2NO$. It is of interest to see if this reaction can take place in ordinary combustion processes to an extent sufficient to affect the accuracy of the calculations in the preceding cases, in which it has been assumed that no formation of NO occurs.

Illustration 9. If cold air is heated at atmospheric pressure to $4000^\circ F$, what percentage of the oxygen in the initial, unreacted air is converted to NO at equilibrium?

Solution. Choose a basis of 1 mol of initial, unreacted air (21% O_2 , 78% N_2 , and 1.0% A). Let the mols of NO at equilibrium be x . The number of mols of N_2 at equilibrium is $0.78 - 0.5x$ and of O_2 , $0.21 - 0.5x$. Since the total mols at equilibrium equals 1, the number of mols of each compound is, in this case, numerically equal to the partial pressure of the compound in atmospheres.

In Fig. 3-14 the abscissa is the reciprocal of temperature in degrees Kelvin, $1/T^\circ K$, or $1.8/(4000 + 460) = 0.000402$. From the figure, one finds that $\log_{10} K_p = 1.22$, where $K_p = p_{O_2}^{1/2} p_{N_2}^{1/2} / p_{NO}$,* and p_{O_2} , p_{N_2} , and p_{NO} are the partial pressures of O_2 , N_2 , and NO, respectively, each expressed in atmospheres. K_p is the antilog of 1.22, or 16.6. At equilibrium, then,

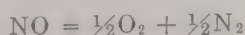
$$(0.21 - 0.5x)^{1/2}(0.78 - 0.5x)^{1/2} = 16.6x$$

Solving this equation gives $x = 0.023$ mol of NO at equilibrium. Since there is no change in volume associated with the reaction, the mols of NO formed are numerically equal to the mols of air reacted, and the initial unreacted air converted to NO must be 0.023 mol. The percentage of the original oxygen converted is $100(0.023/2)/0.21 = 5.5\%$ and that of the nitrogen, 1.5%. Because the heat of formation of NO is 21,600 cal

¹ L. S. Kassel, *J. Am. Chem. Soc.*, **55**, 1351 (1933).

² B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," The Macmillan Company, New York, 1938.

* The equilibrium, or dissociation, constant is for the reaction when written



absorbed per gram mol of NO formed,¹ the reaction lowers flame temperature. On a basis of 1 g mol of air, the heat effect due to formation of NO would, therefore, under the conditions of this illustration, be

$$(0.023)21,600 = 497 \text{ cal}$$

From Fig. 1-3 the sensible heat of 1 g mol of air at 4000°F is

$$8.1(4000 - 60)/1.8 = 17,700 \text{ cal}$$

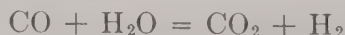
If one assumes that 17,700 cal has been added to 1 g mol of air initially at 60°F, then the final temperature calculated without taking account of NO would be 4000°F, whereas the temperature computed by taking account of NO formation would be approximately equal to

$$60 + (4000 - 60)(17,700 - 497)/17,700 = 3890^\circ\text{F}$$

In other words, at a temperature level of 4000°F, the effect of NO formation on air temperature is to make it roughly 100 Fahrenheit degrees lower than would otherwise be expected. However, the lesser oxygen concentration of combustion gases lessens the NO formation because of the effect on the equilibrium.

As a practical matter, the conclusion to be drawn is that 4000°F is the temperature at which heat effects due to NO formation are beginning to be important. At higher temperatures, the equilibrium becomes more favorable to NO formation and the rate of reaction increases rapidly, so that the effect of temperature may become a very significant factor in the engineering of a process. At temperatures below 4000°F, the less favorable equilibrium and lower reaction rate mean that one is usually safe in neglecting formation of NO; this is doubly true because of the fact that in most flue gases, unless a large excess of air has been used in combustion, the percentage of O₂ is far less than in air.

Frozen equilibria. In an internal-combustion engine the entire cycle of operations almost always completes itself in a small fraction of a second. The expansion of the gaseous products of combustion occurs in a time much shorter still. This expansion cools the gases greatly. At the high temperature levels, not only of combustion but during the early stages of expansion, the rate of the so-called water-gas reaction,



is sufficiently high to maintain substantial equilibrium of the reaction. However, this rate falls rapidly as the temperature decreases. Meanwhile, temperature drop during expansion is so precipitate that the reac-

¹ G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923. Heats of formation of chemical substances are also available in many handbooks.

tion practically ceases. While the slowing of the reaction is not instantaneous but progressive, it is nevertheless sufficiently rapid so that one can as a good approximation treat the case as though equilibrium were maintained down to a definite temperature level, below which no further reaction occurs. Such behavior is spoken of as a "frozen" equilibrium. The temperature corresponding to this freezing depends on equipment and operating conditions.

Illustration 10. An internal-combustion engine burns an oil of 88% C and 12% H by weight, with an air/fuel ratio of 12.8 lb of dry air per pound of fuel.

The design and operation of this engine are such that (1) combustion results in complete elimination of any hydrocarbons from the combustion product, and (2) the water-gas equilibrium in those products is frozen at a temperature level of 1500°F. Exhaust is at atmospheric pressure. What is the gas analysis of the exhaust gas from the unit?

Basis: 100 lb oil.

The number of atoms of carbon in the fuel is 7.33, and that of hydrogen, 11.9. The air supply is 44.13 mols \approx 18.55 atoms O + 34.86 mols N₂. Let the mols of CO₂ = x ; then the mols of CO = 7.33 - x . Let the mols of H₂O = y ; then the mols of H₂ = 5.95 - y , and

$$K_p = x(5.95 - y)/(7.33 - x)y$$

From Fig. 3-14, $K_p = 1.04$. Note that the molal quantities may be equated to K_p in this case, because there is no change in the total number of mols. If there were, molal concentrations would have to be used.

From an O₂ balance, $2x + (7.33 - x) + y = 18.55$, or $x + y = 11.22$.

Solving these two equations, one finds that $x = 6.129$. This corresponds to a gas analysis of 12.71% CO₂, 10.58% H₂O, 2.49% CO, and 1.78% H₂, the remainder being nitrogen.

The best way to solve the equations is probably by trial. If the quadratic equation is used, one has to carry five or six significant figures in the calculations, because the difference between two numbers that are almost equal is involved.

Dissociation of CO₂ and H₂O. Chemical operations sometimes require the use of flames sufficiently hot to cause appreciable dissociation of CO₂ and H₂O in the combustion products, according to the reactions $\text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2$, $\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2}\text{O}_2$ and $\text{H}_2\text{O} = \frac{1}{2}\text{H}_2 + \text{OH}$. At these temperature levels, formation of NO by the reaction



must also be considered. At higher temperature levels, dissociation of hydrogen and oxygen to the atomic state becomes appreciable. The result is that in a gas at equilibrium the relations for several different

reactions must be satisfied simultaneously, making the picture very complicated. However, the basic methods of setting up equations are the same as in a case where only one equilibrium obtains; the complications are chiefly in the numerical solution of the equations.

The equilibrium compositions of a large number of gas mixtures produced by the combustion of carbon, hydrogen, and hydrocarbon fuels have been tabulated by Hottel, Williams, and Satterfield.¹ The following examples illustrate the basic methods of calculation.

Illustration 11. If CO is burnt with the theoretical amount of air, using sufficient preheat to bring the products of combustion to a temperature of 4500°F at normal atmospheric pressure, what is the equilibrium composition of the mixture? Neglect formation of atomic oxygen.

Solution. Choose as a basis 1 mol of CO. The theoretical O₂ is 0.5 mol, while N₂ is $0.5(79/21) = 1.88$ mols. Let x = mols of CO₂ and y = mols O₂ in the equilibrium mixture at 4500°F. By carbon balance, the mols of CO = $1 - x$. By oxygen balance, the mols of NO are

$$1 - x - 2y$$

By nitrogen balance, the mols of N₂ are

$$1.88 - 0.5(1 - x - 2y) = 1.38 + 0.5x + y$$

The total number of mols = $3.38 - 0.5x$. From Fig. 3-14, the values of K_p for the reactions $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$ and $\text{NO} = \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{N}_2$ are 7.9 and 11, respectively, at 4500°F. Inasmuch as the total pressure is 1 atm, partial pressures in atmospheres are numerically equal to mol fractions. Therefore, the equilibrium relations are as follows:

$$\frac{x}{1 - x} \sqrt{\frac{3.38 - 0.5x}{y}} = 7.9$$

$$\frac{\sqrt{y(1.38 + 0.5x + y)}}{1 - x - 2y} = 11$$

In the most general case, each equation in a pair of this sort represents a relation between the two variables, y and x , which in turn corresponds to a curve of y against x . The solution to the simultaneous equations is the pair of values for y and x corresponding to the intersection of these two curves. By assuming some specific value of x , each equation simplifies to one in y only, which can be solved for y . Where the equation is complicated in form it may be necessary, after assuming a value of x , to solve for y by trial and error. If either of the two equations can be solved algebraically for one of the variables expressed as an explicit func-

¹ H. C. Hottel, G. C. Williams, and C. N. Satterfield, "Thermodynamic Charts for Combustion Processes," John Wiley & Sons, Inc., New York, 1949. This reference also includes data on the enthalpy of combustion gases at equilibrium.

tion of the other, it usually pays to do so. If both equations can be solved for the same variable expressed explicitly in terms of the other, equating these two expressions gives an equation in the other variable only. This may be solvable algebraically for the second variable; if so, the whole problem becomes solvable without using either graphs or successive approximations. In the worst event the problem may be solved by assuming a specific value of x , solving each equation for y (employing trial and error if necessary), and repeating the process until each equation yields the same value for y . In doing this, one must be on the watch for multiple roots and analogous algebraic complications.

Where one of the original pair of equations is too complicated for solution for either of the variables (whether the other is or not), the following technique will be found helpful. Solve the simpler of the original pair of equations for corresponding values of the variables, y and x , by whatever technique is best. Whatever the form of the other of the two original equations, it can be rearranged into a form, $y = F_2(x, y)$. Now substitute in the right-hand side of this last expression corresponding values of x and y , calculated from the first equation. If one set of these corresponding values happens to be the roots of the original simultaneous equations, the function $F_2(x, y)$ will in fact be found equal to y . Otherwise, it will be equal to another quantity, which may be called y' . Clearly, if one will plot y' against x , the point of intersection of the curve of y' and y will correspond to the desired roots of the original simultaneous equations.

This last technique has been used in the solution of the two equations given above. The first, solved for y , gives

$$y = \frac{x^2(3.38 - 0.5x)}{62.4(1 - x)^2}$$

The second can be written in the form

$$y' = \frac{121(1 - x - 2y)^2}{1.38 + 0.5x + y}$$

The numerical steps involved in solving the equation by getting the data for the construction of Fig. 3-15 are assembled in the following table. The point of intersection of the two curves, corresponding to the roots of the original equation, is at $x = 0.64+$ and $y = 0.155+$.

	Trial						
	1	2	3	4	5	6	7
Assumed value of x ..	0.5	0.6	0.65	0.63	0.64	0.642	0.641
y	0.0501	0.111	0.169	0.143	0.155	0.158	0.156
y'	11.5	2.14	0.0093	0.465	0.163	0.115	0.144

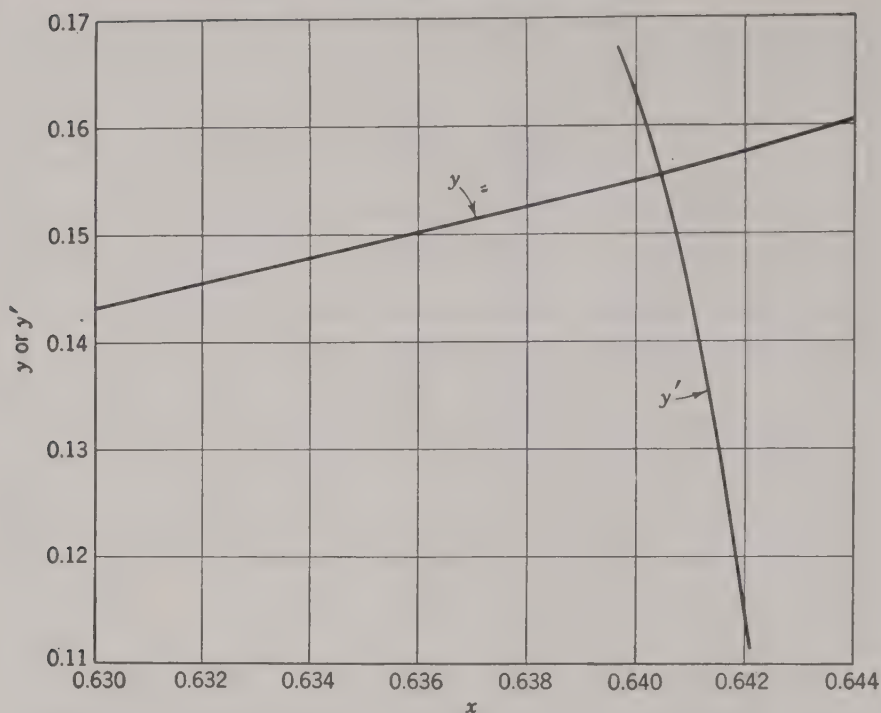


FIG. 3-15. Solution of the two simultaneous equations of Illustration 11.

Using the values of x and y , the composition of the equilibrium gas is computed.

Basis: 1 mol of CO.

Constituent	Mols, function of x, y	Mols	Mol per cent in equilibrium mixture at 4500°F
CO ₂	x	0.640	20.9
CO.....	$1 - x$	0.360	11.8
O ₂	y	0.155	5.1
NO.....	$1 - x - 2y$	0.050	1.6
N ₂	$1.38 + 0.5x + y$	1.855	60.6
Total.....	$3.38 - 0.5x$	3.060	100.0

As a final check on the accuracy of the work, it is wise to substitute the partial pressures in the expressions for the equilibrium constants to see if they give the proper values of K_p .

$$\frac{p_{\text{CO}_2}}{p_{\text{CO}}(p_{\text{O}_2})^{1/2}} = \frac{0.209}{0.118(0.051)^{1/2}} = 7.84$$

$$\frac{p_{\text{O}_2}^{1/2} p_{\text{N}_2}^{1/2}}{p_{\text{NO}}} = \frac{(0.051 \times 0.606)^{1/2}}{0.016} = 11.0$$

The results are in good agreement with the figures of 7.9 and 11 in the original equations, indicating that no significant errors have crept into the manipulation of the equations or the slide-rule work.

Now, turning to inspect the calculated gas analysis and weigh its meaning, one finds that the number of mols of CO left by incomplete combustion to CO_2 is more than seven times the number of mols of NO produced by reaction of N_2 and O_2 , despite the fact that the equilibrium constants for the two reactions are of the same order of magnitude. This emphasizes the point that it is unsafe to judge the degree of completion of a reaction solely on the basis of the equilibrium constant. The concentrations of the various gases and the powers to which they are raised in the expression for the equilibrium constant are important factors that must not be forgotten.

Referring again to the calculated gas analysis, one sees that more than one-third of the CO in the original fuel is unburnt. In other words, more than one-third of the chemical energy obtainable from complete combustion of the original fuel has not been converted to heat. An additional loss has occurred because of the absorption of heat attendant upon the formation of NO. Evidently, at high temperatures the effect of chemical equilibrium in this case is to impose severe restrictions on the availability of chemical energy as heat. As will appear in later chapters, an effect of this sort is characteristic of many chemical reactions.

The final illustration of this chapter indicates the technique of handling the energy relationships when combustion is incomplete.

Illustration 12. If heat losses from the combustion chamber of Illustration 11 to the surroundings are negligible and if the CO and air supplied to the chamber are both preheated to the same temperature, what is the preheat temperature required?

Solution.

Basis: 1 lb mol of CO fuel and theoretical air, originally at 60°F , having chemical energy equal to the heat of combustion of the CO.

On this basis the CO supplied to the combustion chamber is 1 mol, the O_2 is 0.5 mol, and the N_2 is 1.88 mols. Let x = the sensible-heat content of these gases in Btu at the temperature at which they enter the combustion chamber. Their total heat content or enthalpy, then, equals the heat of combustion of 1 mol of CO plus x , or $67,600(1.8) + x$.

To compute the enthalpy of the equilibrium mixture as it leaves the combustion chamber at 4500°F , imagine that 1 mol of CO_2 and 1.88 mols of N_2 at 60°F are converted to the equilibrium mixture at 4500°F by a series of steps, as follows: First, 0.360 mol of CO_2 at 60°F is dissociated to form 0.360 mol of CO and 0.180 mol of O_2 , both at 60°F . Next, 0.025 mol of O_2 and 0.025 mol of N_2 react at 60°F to form 0.050 mol of NO. Finally,

the mixture remaining after these reactions and containing $1 - 0.360 = 0.640$ mol CO_2 , 0.360 mol CO , $0.180 - 0.025 = 0.155$ mol O_2 , 0.050 mol NO , and $1.88 - 0.025 = 1.855$ mols N_2 is heated from 60° to 4500°F . The over-all change in enthalpy is the sum of the changes for each of the three steps.

The above is equivalent to saying that the enthalpy of the equilibrium mixture relative to the chosen basis is the sensible heat of the various constituents above 60°F plus the chemical energy, where the latter is simply the heat of combustion of the CO and the heat of decomposition of the NO , both measured at 60°F . In the present case, the magnitudes and signs of the chemical-energy terms are quite obvious and can be determined without the necessity of writing out the various steps in such detail as in the preceding paragraph. However, in the case of complex mixtures one often may become confused as to just how to treat the chemical-energy terms. The tangle can always be unraveled by breaking the process down into a series of steps such as is outlined above.

From the following table the enthalpy of the equilibrium mixture at 4500°F is seen to be 171,400 Btu:

<i>Gas</i>	<i>Enthalpy, Btu</i>
CO_2 : $0.640 (4500 - 60)(13.4)$	38,100
CO : $0.360 (4500 - 60)(8.2) + (67,600)(1.8)$	57,000
O_2 : $0.155 (4500 - 60)(8.6)$	5,900
NO : $0.050 (4500 - 60)(8.4) + (21,600)(1.8)$	3,800
N_2 : $1.855 (4500 - 60)(8.1)$	66,600
Total.....	171,400

By an energy balance around the combustion chamber,

$$67,600(1.8) + x = 171,400$$

and $x = 49,500$ Btu. By the methods of Illustration 6 (page 79), the preheat temperature is found to be approximately 2000°F .

PROBLEMS

1. CO_2 gas is to be heated at atmospheric pressure. Calculate the following:

(a) The Btu required to heat 1 lb mol from 60°F to 2000°C . *Ans.* 46,000.

(b) The average value of M_{c_p} in the interval from 500°C to 2000°C . *Ans.* 13.8.

2. The flue gases from a calcining furnace contain 11.1% CO_2 , 5.7% O_2 , 0.8% CO , 6.3% H_2O , and the rest N_2 . These gases go to the regenerator, entering the regenerator at the rate of 22,000 cu ft/min at atmospheric pressure and 1700°C . In the regenerator they are cooled to 200°C by countercurrent heat exchange with air.

(a) Compute the sensible-heat content of the flue gases in Btu/hr above a datum of 60°F . *Ans.* 13,200,000.

(b) How many Btu/hr must be abstracted from the flue gases in the regenerator? *Ans.* 12,000,000.

(c) Assuming that the nitrogen in the flue gases comes wholly from the air supplied

to the regenerator at a temperature of 60°F, that the furnace and regenerator are continuous in operation, and that 15% of the heat removed from the flue gases in the regenerator is lost through the regenerator walls, calculate the temperature of the air leaving the regenerator. *Ans.* 1480°C.

3. A large apartment-house boiler uses a high-grade distillate fuel oil with a heating value of 18,700 Btu/lb. The temperature of the air entering the furnace is 65°F. The stack gas leaves at 560°F, and its average analysis is 11.2% CO₂, 0.4% CO, and 6.2% O₂. Assuming that the fuel oil consists only of hydrocarbons and that soot formation is negligible, calculate the following:

- The per cent excess air.
- The composition of the fuel oil.
- The per cent of the heating value of the fuel oil that is lost as sensible heat in the stack gases.

4. A blast-furnace stove is being alternately heated by the combustion of blast-furnace gas and cooled by passing the air blast to the furnace through the stove. During the heating portion of the cycle, blast-furnace gas and air enter the stove at an average temperature of 60°F, while flue gas leaves the stove at a temperature varying substantially linearly with time from 580°F to 780°F. A representative sample of the blast-furnace gas contains 0.3% CH₄, 2.3% H₂, 0.3% O₂, 13.3% CO₂, 25.6% CO, and 58.2% N₂. The average composition of the flue gas is 1.2% O₂, 26.1% CO₂, 0.2% CO, and 72.5% N₂. The heating value of the blast-furnace gas is 92.5 Btu/cu ft at 60°F and 1 atm. On the average, what fraction of the heating value of the blast-furnace gas is carried up the stack as sensible heat in the flue gas?

5. The stack gases from a furnace fired with a high-grade fuel oil analyze 13.9% CO₂, 3.1% O₂, and 83.0% N₂. The air for combustion is essentially dry, and the stack gases are at 600°F and atmospheric pressure. Determine the heat recovery per pound of oil burnt, when the flue gases are cooled to 300°F.

6. A furnace is burning a high-grade oil, and the stack gases from the furnace are used to preheat the entering air by countercurrent exchange. The stack gases analyze 10.0% CO₂, 6.8% O₂, and 83.2% N₂. The air enters the preheater at 60°F and cools the stack gases from 1000°F to 600°F. Neglecting heat losses to the surroundings, calculate the temperature of the air leaving the preheater.

7. A petroleum refiner plans to cool 850 lb mols/hr of hot hydrocarbon gases by heat exchange with 140,000 lb/hr of gas oil in a parallel-flow heat exchanger. The hot gases will enter the exchanger at 800°F. The gas oil is available at 60°F. Information on the thermal properties of the two streams is summarized below.

Temperature, °F	Enthalpy relative to 60°F	
	Gas stream, Btu/lb mol	Gas oil, Btu/lb
100	1,000	17
200	3,500	64
300	6,000	117
400	10,500	175
500	18,200	238
600	31,100	307
700	40,900	381
800	48,100	461

What is the lowest temperature to which the gases can be cooled by the proposed arrangement? What will this temperature be if the gas stream enters the exchanger at 600° instead of 800°F?

8. A plant is proposing to utilize waste gas, now being discarded at 750°F, to supply the heat for a waste-heat boiler, which is to produce saturated steam at 400°F from feedwater at 70°F. The average molal heat capacity of the gas is 8.2. Under ideal conditions, *i.e.*, no heat losses to the surroundings and very large heat-exchange surfaces, what is the maximum possible production of steam, expressed as pounds of steam per pound mol of gas?

9. Moist hot air at 280°F, carrying 0.3 lb steam per pound of dry air, enters the top of a counterflow heat exchanger with vertical tubes and flows down the inside of the tubes. The cooled air and condensed steam flow out the bottom of the tubes. Around the tubes flows upward a stream of dry air, entering at 60°F. The gases on both sides flow at substantially 15 psig, with a flow rate of 80 lb/min of dry air (with its accompanying steam) on the inside and 650 lb/min on the outside of the tubes. What per cent of the steam entering this unit is it possible to condense in it? Neglect heat losses to the surroundings and any radial temperature gradient in either stream. Assume that the average specific heat of air is 0.24.

10. In each of the cases below, determine the theoretical flame temperature in degrees Fahrenheit. Assume that both fuel and air are supplied to the combustion chamber at 60°F. Neglect formation of NO and dissociation of CO₂ and H₂O.

(a) Combustion of amorphous carbon with the theoretical amount of air to form CO₂. Ans. 4050°F.

(b) Combustion of amorphous carbon with the theoretical amount of air to form CO.

(c) Combustion of rhombic sulfur to SO₂, employing 100% excess air, computed on the basis of the theoretical amount required to form SO₂ (see Fig. 6-1, p. 168).

(d) Combustion of H₂ with 140% of theoretical air. Ans. 3240°F.

(e) Combustion of H₂ with oxygen-enriched air containing 30% O₂, employing 140% of the theoretical amount of O₂.

(f) Combustion of H₂ with an amount of air such that the products of combustion contain N₂ and H₂ in the correct stoichiometric proportions for synthesis of ammonia.

11. If the excess air supplied to the combustion chamber of Illustration 6 is increased from 50% to 100%, to what temperature is it necessary to preheat the air and fuel?

12. A furnace is fired with a fuel oil containing 83% C and substantially free from sulfur and nitrogen. The air used for combustion enters at 85°F and with a partial pressure of water vapor of 26 mm. The flue gas contains 10.5% CO₂, 0.6% CO, and 6.0% O₂ (Orsat analysis over mercury). The stack gases leave the furnace at a temperature of 840°F and under a draft of 1.6 in. of water. The oil as fired has a heating value of 20,220 Btu/lb. The barometer is 748 mm. Per pound of fuel fired, compute the following:

(a) Cubic feet of free air entering the furnace. Ans. 274.

(b) Cubic feet of stack gases leaving the furnace. Ans. 691.

(c) Btu lost in the stack gases as a result of unburnt CO. Ans. 455.

(d) Btu lost in the stack gases as sensible heat. Ans. 4100.

(e) Btu lost in the stack gases as a result of failure to condense the water formed upon combustion of the hydrogen in the fuel. Ans. 1267.

(f) Btu recoverable from the stack gases by cooling them by means of a heat exchanger to 300°F. Ans. 2970.

(g) Btu otherwise lost which would be recoverable by reducing the excess air to 10%, on the assumption that the percentage of the total carbon burnt that goes to CO remains the same as at present. Ans. 660.

(h) Temperature to which the entering air would be preheated in the exchanger of

part (f) if the wall and other losses (by conduction, radiation, etc.) amount to 22% of the heat given up by the stack gases in passing through the exchanger. *Ans.* 566°F.

13. The heat of combustion of the fuel oil of Illustration 6, Chap. 2, is 19,500 Btu/lb. The moisture content of the air used for combustion is 12 mm, the barometer 750 mm, and the temperature 65°F. The temperature of the exhaust gas is 1420°F. What percentage of the lower heating value of the fuel used is lost as unutilized chemical heat (also lower heating value) in the exhaust gases and what as sensible heat in these gases above 65°F?

14. Flue gas leaves a reheating furnace at 1500°F with the following analysis: 11.1% CO₂, 1.2% CO, 5.1% O₂, and 82.6% N₂. This gas passes through a brickwork duct to a waste-heat boiler. It leaves the boiler at 720°F and now contains 10.19% CO₂ and 0.31% CO. The fuel for the reheating furnace is an oil containing only carbon and hydrogen in appreciable amounts. Soot formation and the amounts of unburnt gases other than CO are negligible. Calculate the total heat absorption of the waste-heat boiler plus the heat lost by the boiler and duct to the surroundings per pound of oil fired.

15. A gas reaction conducted in metal tubes packed with catalyst absorbs 20,000,000 Btu/hr. The tubes are heated by direct contact with combustion gases, the product of burning CO with 80% of the theoretical air. On account of the metallurgical characteristics of the tubes, the temperature of the heating gases in contact with them must never exceed 1200°F. At the same time, in order for the catalytic reaction to take place within the tubes, the temperature of the heating gases must be at least 1000°F. Under normal operating conditions the heating gases withdrawn from the reactor are at 1000°F, and a portion of these gases is recycled and mixed with the gases leaving the CO combustion chamber in order to reduce the temperature of the gases entering the reactor to 1200°F.

The CO is burnt in a combustion chamber lined with firebrick. The characteristics of the firebrick limit the temperature of the combustion chamber and make it inadvisable to have the combustion gas leave the chamber at a temperature above 3000°F. To maintain this temperature without wasting any heat, a steam generator is installed in the chamber to generate saturated steam at a pressure of 450 psig.

Part of the sensible heat of the combustion gases leaving the reactor is recovered by heat exchange with the air used for combustion. The temperature of the air entering the exchanger, the CO entering the combustion chamber, and the boiler feed-water is 60°F, and the exhaust gas leaves the exchanger at 450°F. The amount of free O₂ in the gases leaving the combustion chamber is negligible. Calculate the following:

- The composition of the exhaust gas leaving the heat exchanger.
- Mols of CO fired per hour.
- Mols of recycle gas per hour.
- Mols of air used per hour.
- The temperature of the preheated air.
- Mols of exhaust gas per hour.
- Pounds of steam generated per hour.

16. Solve Illustration 9, assuming that the air employed as the starting material is replaced by oxygen-enriched air containing

- 40% O₂, 60% N₂ and A.
- 60% O₂, 40% N₂ and A.
- 80% O₂, 20% N₂ and A.

What should the percentage of oxygen in the starting material be to yield the maximum possible conversion of oxygen in the starting material to NO? To yield the maximum possible concentration of NO in the equilibrium mixture at 4000°F?

17. A high-grade fuel oil containing 91% C and 9% H is burnt in an internal-combustion engine. Operation is smooth, and there is no smoke production. Orsat analysis of the exhaust gases over mercury shows 15.25% CO_2 and 2.98% CO. If one assumes the existence of a frozen equilibrium in this engine, at what temperature did the freezing occur?

18. Pure methane gas is mixed with 95% of the theoretical air and fed into the cylinder of an Otto-cycle internal-combustion engine. At a given point in the engine cycle, the pressure and the temperature in the cylinder are 30 atm abs and 2000°F , respectively. If the combustion products are in chemical equilibrium at this point and the gas laws are valid, what is the composition of the gas in the cylinder on the wet basis? The assumption that no carbon or methane is present is justified.

19. Solve Illustration 11, assuming 40% excess air instead of theoretical air.

20. CO is to be burnt with air at atmospheric pressure to produce a gas in which the molal ratio of CO to CO_2 is 1. The combustion will take place in a well-insulated chamber, and the products of combustion are to leave this chamber at a temperature of 4400°F . CO will enter the furnace at 60°F , while the air will be preheated to whatever temperature is necessary to give the desired flue-gas temperature. Assume that the only significant reaction is the oxidation of CO.

(a) What will be the composition of the gas leaving the combustion chamber?

(b) What per cent of the theoretical air must be supplied to the furnace?

(c) To what temperature must the air be preheated?

21. As a step in the production of nitrogen oxide, a dry mixture of 50% nitrogen and 50% oxygen is to be heated at atmospheric pressure from 600°F to a high temperature, which may reach 4400°F . Plot the heat consumption of this operation, expressed as Btu per pound mol of NO formed, as a function of the temperature level to which the mixture is heated. Repeat the construction of this curve for an initial mixture of 30% oxygen and 70% nitrogen and for one of 70% oxygen and 30% nitrogen. Discuss constructively the significance of the curves from the point of view of the process in question.

22. A plant has a spent granular catalyst contaminated with 4 wt-% of carbon, which must be removed by burning off with air. The catalyst flows down through a regenerating chamber as a uniform, moving bed of granules, up through which counterflows the O_2 -containing gas. To prevent excessive temperature rise, which would ruin the catalyst, the air is diluted with recycled spent O_2 -free gas leaving the unit. To ensure good reaction conditions, the diluted O_2 -containing gas enters the bottom of the unit at 800°F , while the granules enter the top at 900°F . The maximum temperature in the unit must not exceed 1000°F .

(a) What per cent O_2 do you recommend in the gas entering the unit? Assume that combustion goes completely to CO_2 .

(b) What per cent O_2 do you recommend if the original carbon contamination is only 0.4 wt-%? Assume that combustion goes completely to CO_2 .

(c) What per cent O_2 do you recommend if the original carbon is 4%, but on combustion 24% of the carbon goes to CO and the rest to CO_2 , with no further reaction above the combustion zone?

(d) What would you expect to happen if a zone of granules in the shape of a horizontal lens of permeability to gas somewhat lower than that of the rest of the bed were to form at the top of the bed and move down with and through it as the flow of the granules proceeds? Why?

(e) If the location of the combustion zone starts to move vertically upward through the bed, what will you do?

(f) If the temperature of the combustion zone starts to rise, what will you do?

(g) Sketch the temperature gradients through the bed.

Attention is called to the following characteristics of the operation: (1) The catalyst particle size is small enough (*i.e.*, the ratio of surface to weight is high enough) so that heat exchange between gas and catalyst is very rapid. (2) When the O_2 in the gas actually meets the carbon-containing catalyst, combustion goes on so rapidly that it is completed in a very thin layer of the catalyst bed, *i.e.*, no O_2 is consumed any significant distance below this zone or layer, and no O_2 as such is left in the gas any significant distance above this zone. Moreover, while the thermal conductivity of the catalyst bed is low enough so that heat flow in a vertical direction is negligible for the bed as a whole, the conductivity is enough so that heat distribution in the very thin combustion zone itself is so complete that no significant temperature gradient through it in a vertical direction is measurable. (3) In the temperature range involved, the specific heat of the catalyst is 0.4.

Chapter 4

SOLID FUELS

Composition of solid fuels. Unlike gaseous and liquid fuels, most solid fuels (with the exception of petroleum cokes) contain appreciable percentages of mineral compounds. It is also true that the moisture content is often considerably higher than is characteristic of gases and liquids. In the latter, in the absence of emulsified water, the moisture content is limited to a relatively low value by the solubility of water in oils; while in the case of solid fuels, moisture can be bound to the surface by adsorptive forces or held mechanically in the pores and crevices. Otherwise, the chemical elements present in solid fuels are the same as those in gaseous and liquid.

Ultimate analysis. In the ultimate analysis of solid fuels carbon, hydrogen, sulfur, nitrogen, and ash (*i.e.*, the mineral residue resulting from complete combustion of the fuel) are normally determined and reported. Oxygen, when reported, is usually found by difference.¹ The ultimate analysis may be reported upon either a dry, "air-dried," or "as-fired" basis.

The normal use made of the ultimate analysis of an organic compound is to determine purity or structure of the compound. Because of the extraordinary complexity of structure of solid fuels, it is impossible to use the analysis in this way. However, as will appear in the following pages, the analysis is indispensable in setting up essential material balances in the industrial processes in which the fuels are employed. In using the data thus, they are often interpreted in ways that are conventional and arbitrary but which are justified on the basis of convenience. The student should keep in mind the limitations of the data.

The data of the ultimate analysis are conveniently rearranged as follows:

1. Moisture (loss in weight at 105°C).
2. Combined water, equivalent to the oxygen of the ultimate analysis
3. Carbon

¹ For details of methods of analysis, refer to ASTM Standards, Part III, 1940 Supplement.

4. Available or net hydrogen (hydrogen other than that in moisture and combined water)
5. Sulfur and nitrogen (usually in small amounts)
6. Ash

The term "combined water" is used variously. It may or may not include moisture. The usage should be clearly indicated, by choice of basis or otherwise.

In fuel calculations, the sulfur and nitrogen are often neglected (except in the calculation of the oxygen in the fuel by difference), though present in amounts ranging from 1 to 3% or more.

Since the hydrogen content is always in excess of that necessary to form water with the oxygen, it can be assumed for purposes of calculation that all the oxygen is present in the form of water of chemical combination; the excess of hydrogen is then termed "available" or "net," *i.e.*, combustible or burnable hydrogen.

Net hydrogen. This arbitrary term is usually defined as the total hydrogen in the coal less the hydrogen equivalent to the available oxygen (found by difference) in the coal. This implies that the mineral constituents of the fuel, including all their oxygen, are inert and that the hydrogen and available oxygen are in the organic matter of the coal. Since the oxygen is evaluated by difference, the percentage reported and, consequently, the calculated "net" hydrogen are affected by all the errors incurred in the other determinations. Also the change in weight undergone by the mineral constituents upon ignition to ash influences these values, the combustion of FeS_2 to Fe_2O_3 exerting the major effect (although its magnitude is small). Loss of water of formation by clayey and shaly materials and of CO_2 by carbonates occurs but is usually small. In other words, the ash "as weighed" does not truly represent the mineral content as it occurs in the fuel itself, and thus the oxygen by difference does not represent the organic oxygen of the true fuel substance. Since the net hydrogen is dependent upon the value reported for oxygen, it is apparent that this quantity may be reported as either of two values, depending upon the interpretation given to the ash analysis.

In the light of the above, a correction is sometimes made to the ash value. Consider the case of a coal containing pyritic sulfur, the iron in the pyrites appearing in the ash as Fe_2O_3 , the combustion equation being $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$. For each 8 atoms of this sulfur, 6 atoms of oxygen combine with the iron. If this oxygen is assumed to be derived from the organic oxygen in the coal substance rather than supplied by air, then the oxygen actually existing in the organic matter of the coal is greater than the "available" oxygen found by difference by an amount equal to the oxygen which finally ends up in combination with the iron, namely, $6(16)/8(32) = 3/8$ ths the pyritic sulfur. Granting

that all other inorganic constituents in the ash existed in the original coal in the same form as they appear in the ash,¹ it follows that the organic oxygen is the oxygen obtained by difference increased by 3/8ths the pyritic sulfur. Were net hydrogen defined as total hydrogen less the hydrogen equivalent to the organic oxygen, the value of net hydrogen obtained conventionally would also have to be decreased by 2/16ths times 3/8ths the pyritic sulfur. However, if one wishes to compute on this basis the oxygen theoretically required to burn the fuel, one must furnish enough oxygen from the air to burn the net hydrogen thus computed and also an additional amount to combine with the iron of the pyrites. On the other hand, if this theoretical oxygen requirement is computed without correcting the ash as above, the value obtained will be numerically equal to that when making the correction, since both the net hydrogen calculated on the uncorrected basis and the oxygen required to burn it are larger than in the corrected case by an amount equivalent to the oxygen necessary to combine with the iron in the ash. It is, therefore, stoichiometrically simpler not to correct the ash and to assume that all the oxygen required to form the Fe_2O_3 comes from the oxygen of the coal (equivalent to assuming that the iron exists as Fe_2O_3 in the fuel substance and thus remains unchanged during combustion). *Net hydrogen* may therefore be defined as *that hydrogen for which oxygen from the air must be supplied for its combustion*. Such a definition is entirely justified, since experience has shown that the value of oxygen obtained by difference is always a positive value, *i.e.*, the oxygen of the coal is always in excess of that required for the combustion of pyrites to Fe_2O_3 .

Since total sulfur is reported separately, the oxygen by difference is in error unless the ash is in fact free of sulfur, for otherwise the sulfur in the ash would be counted twice. Where pyritic sulfur is present in the coal some of it always remains in the ash, but the amount is usually small enough to neglect. The correction may become important where the sulfur is high and the ash is basic in character.

Proximate analysis. This important method of laboratory examination of solid fuels is based upon their volatilization characteristics. It involves determination of moisture, volatile combustible matter, non-volatile combustible matter, and ash. The loss in weight experienced by a sample when heated for 1 hr at 104 to 110°C* is reported as moisture content. Upon ignition in a covered crucible for 7 min at 950°C, the dried sample loses most of its combined water and hydrogen and a large amount of carbon (*e.g.*, in the form of volatile hydrocarbons), leaving the ash and the residual carbon. This loss is called "volatile combustible

¹ This assumption, as is pointed out above, is rarely entirely justified, but it seldom leads to serious error.

* ASTM Standards, *op. cit.*

matter." The combustible left after this ignition is called "fixed carbon." The ash is the residue left from complete combustion of the sample in the open air at 725°C. The sum of moisture, volatile combustible matter, fixed carbon, and ash is, therefore, 100%.

The proximate and ultimate analyses of a Pennsylvania coal are given as follows, both being on an "air-dried" basis:

	<i>Proximate per cent</i>		<i>Ultimate per cent</i>
Moisture.....	3.2	Carbon.....	79.90
Volatile combustible matter....	21.0	Hydrogen.....	4.85
Fixed carbon.....	69.3	Sulfur.....	0.69
Ash.....	6.5	Nitrogen.....	1.30
		Ash.....	6.50
		Oxygen (by difference).....	6.76
Total.....	100.0	Total.....	100.00

These two analyses must never be confused. From the proximate analysis it should not be concluded that the per cent of carbon in the coal is 69.3, for it must be remembered that the volatile matter contains carbon, enough in this case to make the total 79.90%. Likewise, the difference of 6.76% between the total of the ultimate analysis as directly determined and 100% should not be called combined water. This difference is assumed to be oxygen. The hydrogen equivalent to the 6.76 of oxygen is $6.76(2/16) = 0.85$, leaving 4.00 as the available or net hydrogen, and $6.76 + 0.85 = 7.61$ as the total of combined water and moisture. Since, from the proximate analysis, it is already known that the moisture is 3.2, the combined water is 4.41%

In making combustion calculations it must be emphasized that when reliable results are desired, a knowledge of the ultimate analysis is essential. In order to obtain by a material balance a correlation between the analysis of the fuel and that of the products of combustion (*e.g.*, to determine the volume of combustion gases per unit weight of fuel fired), the relative amounts of some constituent common to both analyses must be known. The conventional method of determining this ratio has long been the use of a carbon balance. In other words, all the carbon in the fuel shows up in the stack gas, except for one form or another of unburnt combustible and possible leakages of combustion gases from the furnace. Thus the total carbon of the fuel must be known in order that such a balance may be used. However, because the ultimate analysis of coal is tedious and expensive, it is often omitted, the proximate analysis being substituted for it. Under these circumstances there are several methods for estimating the total carbon of the fuel which, though only approximate, are satisfactory for many engineering purposes. The estimations

are based on various empirical relations, such as the Calderwood¹ or the Dulong² equations. In addition to the proximate analysis, the higher heating value and the weight per cent of sulfur of the coal are also required. Both of these are easily determined and are usually reported with the proximate analysis.

Dulong Formula.

$$\text{Btu/lb} = 14,544C + 62,028(H - O/8) + 4050S$$

where Btu/lb = higher heating value

C = weight fraction of carbon

S = weight fraction of sulfur

$H - O/8$ = weight fraction of net hydrogen = total hydrogen - $1/8$ oxygen

This equation may be used in conjunction with the flue-gas analysis for the calculation of the per cent carbon in the coal, the flue-gas analysis giving the ratio of net hydrogen to carbon. Its coefficients assume negligible heat of formation of the organic matter from the elements. Their values are based on the heats of combustion of the elements involved.

Calderwood Equation.

$$C = 5.88 + 0.00512(B - 40.5S) \pm 0.0053 [80 - 100(\text{VCM}/\text{FC})]^{1.55}$$

where S = sulfur as weight per cent of the coal

B = higher heating value in Btu per pound of coal

VCM = volatile combustible matter in weight per cent of coal

FC = fixed carbon as weight per cent of coal

C = carbon as weight per cent of coal

The sign of the last term is taken as negative if $100 (\text{VCM}/\text{FC})$ is greater than 80. The percentages are expressed on an "air-dried" basis, but the error introduced by using a basis with any reasonable moisture content or even by using a moisture- and ash-free basis is usually negligible.

The Calderwood equation is particularly applicable to bituminous coals, for which it was originally intended. For other grades of coal it has been found to apply with very few exceptions with an error of not more than 2%.

Where the origin of the coal in question is known, it is usually safe to assume that the ultimate analysis of its *total combustible matter* is identical with that of other samples from the same field, particularly from the same vein. Tables listing such analyses for all important fields in the United States are issued from time to time by the U.S. Bureau of Mines.³

¹ J. P. Calderwood, *Penn. State Coll. Bull.* 14, 1917.

² H. H. Lowry (ed.), "Chemistry of Coal Utilization," Chap. 4, by W. S. Selvig and F. H. Gibson, John Wiley & Sons, Inc., New York, 1945.

³ *U.S. Bur. Mines Bulls.* 123, 193, etc.

Unburnt combustible. In the illustrations of Chaps. 2 and 3, the fuel was assumed to be completely gasified by combustion, an assumption usually justified when oil and fuel gases are under consideration and often when solids are the combustible material. This assumption may, however, lead to serious error in the case of the latter, because the furnace ashes often contain a considerable amount of combustible matter.

Since the mineral constituents of the fuel are known chemically as *ash*, it is common practice to designate the ashes removed from the furnace as "refuse," which may include varying amounts of unburnt combustible matter. This latter is generally one of two kinds, depending upon the type of grate and the method of firing employed. With some grates and coals the finer particles of fuel fall through before any appreciable heating has taken place, but the refuse is otherwise well burnt out. Here the combustible matter in the refuse is of the same composition as the original fuel. With other types, all the fuel is thoroughly coked before any can escape into the ash pit, so that any unburnt combustible is essentially carbon. From the character of the grate and coal and an examination of the refuse it is usually possible to decide to which class the case belongs. There are, of course, gradations between these two extremes, and if the amount of unburnt matter in the ashes appears large enough to affect the combustion calculations, a complete analysis should be made.

Illustration 1. If a coal with a heating value of 14,350 Btu/lb contains 37.0% volatile matter, 40.5% fixed carbon, and 8.9% ash and the refuse left after combustion contains 7.4% volatile matter, 8.25% fixed carbon, and the rest ash, it can be seen by inspection that this is a case of unburnt coal actually falling through the grate, since the ratio of fixed carbon to volatile matter in the fuel, $40.5/37.0 = 1.094$, is practically the same as the ratio, $8.25/7.4 = 1.114$, in the refuse. The ash in the original fuel passes through the grate unchanged and can be used as the basis for any comparison. The ratio, pounds of combustible per pound of ash, in the fuel is $(37.0 + 40.5)/8.9 = 8.71$, whereas in the refuse it is

$$(7.4 + 8.25)/(100 - 7.4 - 8.25) = 0.186$$

Consequently, the ratio of the amount left to the total amount,

$$0.186/8.71 = 0.021$$

represents that fraction of the coal not burnt and therefore the fraction of the heating value lost from this cause.

Suppose, however, the same coal be burnt under conditions such that analysis of the dry refuse shows 0.4% volatile matter and 15.6% fixed carbon. Here it is apparent that the fuel has been thoroughly coked but the coke incompletely burnt.¹ Since, in the process of coking, the fuel

¹ Even pure carbon shows a trace of volatile matter as the analysis is carried out.

has lost some of its combustible and its corresponding heating value, a direct comparison cannot be made as above. However, the heating value of the carbon in the refuse may be found as follows:

Basis: 1 lb coal.

Lb ash	Lb C in refuse	Atoms C	Chu available	
0.089	16		97,000	$\frac{1.8}{14,350} = 247$ Btu loss per pound coal
	84	12		

The loss in the heating value is, therefore, $(247/14,350)100 = 1.72\%$.

Illustration 2. A coal contains 4% moisture, 23% volatile matter, 64% fixed carbon, and 9% ash and has a heating value of 14,100 Btu/lb. Determination of the carbon in the coal shows it to be 79%. The refuse removed from the ash pit of a grate-fired furnace using this coal contains 62% moisture (due to wetting down of the ashes by the hose to lay dust), 3% volatile combustible matter, 11% fixed carbon, and 24% ash. Estimate the per cent of the heating value of this coal lost in the furnace as unburnt combustible and the per cent of carbon fired which remains in the refuse.

Solution. The combustible matter in the refuse is not wholly coked fuel, as is evidenced by the presence of considerable volatile matter in it; neither is it wholly uncoked coal, since the ratio of fixed carbon to volatile in the fuel, $64/23 = 2.78$, is not the same as that, $11/3 = 3.67$, obtained from the refuse. It is fair to assume that some wholly unburnt coal has dropped through the grate, the amount of this being measured by the volatile matter in the refuse, and that additional coal, coked completely in passing over the grate, has not had all the carbon burnt out of it. These are reasonable assumptions, since in the actual coking process there is little loss of volatile matter until a certain temperature is reached, but when decomposition starts it is completed in a relatively narrow temperature range without much further heat supply and, on a furnace grate, in a relatively short time.

The volatile combustible matter in the refuse is a measure of and is proportional to the uncoked coal. Therefore the loss in heating value due to uncoked coal is estimated as follows:

Basis: 1 lb coal as fired.

Lb ash	Lb volatile in refuse		
0.09	3	100	$\frac{100}{23} = 0.049$ lb uncoked coal in refuse
	24	23	

There is a corresponding loss in heating value of $(0.049)14,100 = 690$ Btu.

The total fixed carbon in the refuse is made up of that due to uncoked coal as well as that from the coke present. The former, expressed per 100 lb of refuse, is $3 \times 64/23 = 8.35$ lb, whereas the difference, $11 - 8.35 = 2.65$ lb, is that corresponding to the coke present. That is, the number of pounds of carbon in the refuse is $0.09(2.65/24) = 0.0099$ per pound of coal and the corresponding heating value is

$$(0.0099/12)(97,000)1.8 = 145 \text{ Btu}$$

Therefore, the total per cent loss is $(690 + 145)(100)/14,100 = 5.92\%$.

In these computations the presence of moisture in the refuse introduces no complications, since ratios alone are used to transform from one basis to another.

If there is 0.049 lb of uncoked coal in the refuse, there is $0.049(0.79) = 0.0387$ lb of carbon in it. The total carbon unburnt is $0.0387 + 0.0099 = 0.0486$ lb, or $100(0.0486/0.79) = 6.15\%$ of the carbon in the coal.

Sulfur in ash. The combustion stoichiometry of high-sulfur solid fuels is complicated somewhat by the effect of the ash. In general, a part of the sulfur remains in the ash, and where the sulfur content of the fuel is high, it may occasionally be necessary to allow for this. Stoichiometrically, such sulfur plays no part in combustion. Total sulfur less that in the ash may, therefore, be called "net" or combustible sulfur. Since oxygen in the coal is obtained by difference, in computing it only net sulfur should be used, since otherwise sulfur in the ash would be counted twice.¹ Furthermore, net sulfur requires oxygen to burn it. Whether this be assumed to come from the oxygen of the coal or from the air is stoichiometrically immaterial, but it is perhaps simpler to assume the latter, thereby counting the available oxygen as combined water and computing the net hydrogen on this basis. The amount of oxygen required for the net sulfur depends on the extent to which the SO_2 is oxidized to SO_3 . While this always occurs to some extent, it is usually allowable to neglect the oxidation beyond the SO_2 stage.

Illustration 3. A furnace uses a coal the ultimate analysis of which shows 57.22% C, 5.64% H, 1.41% N, 5.06% S, and 14.67% ash. The combustible matter left in the ash from the furnace is negligible. The ash of this particular coal is found by analysis to contain 9.62% S. On the assumption that this furnace secures complete combustion, using 80% excess air, all the sulfur in the combustion gases appearing as SO_2 , compute the Orsat analysis of the combustion gases, if the sample be collected

¹ However, as is stated on p. 102, correction of the ultimate analysis for the sulfur in the ash is not usually made.

through a tube filled with PbO_2 (which quantitatively removes SO_2). What is the per cent net hydrogen in this fuel? What would be the computed per cent net hydrogen if, as is normally the case, the sulfur in the ash were neglected?

Solution. The sulfur determined by analysis is the total sulfur. Since part of it remains in the ash, part of it belongs there when arranging the results of the analysis. Taking a basis of 100 lb of coal, this amount is $14.67(0.0962) = 1.41$ lb, included in the ash as determined. The remainder of the sulfur, $5.06 - 1.41 = 3.65$ lb, is the sulfur converted to SO_2 , *i.e.*, the "net" sulfur. Arranging the analysis in tabular form, using the value 3.65 for sulfur, one obtains the oxygen by difference, which is equivalent to combined water.

Basis: 100 lb coal.

	Pounds	Mols or atoms
C.....	57.22	4.77
H ₂	5.64	2.79
N.....	1.41	
Net S.....	3.65	0.114
Ash.....	14.67	
O (by difference).....	17.41	1.088
Total.....	100.00	

Net H₂, $2.79 - 1.088 = 1.70$ mols

Net H₂, $1.70(2.02) = 3.43$ lb, or 3.43 %

O₂ for theoretical combustion, $4.77 + 0.114 + 1.70/2 = 5.73$ mols

Excess O₂, $0.80(5.73) = 4.58$ mols

N₂ from air, $(5.73 + 4.58)(79/21) = 38.8$ mols

Flue gas (dry, SO_2 -free) contains:

Gas	Mols	Per cent
CO ₂	4.77	9.9
O ₂	4.58	9.5
N ₂	38.8	80.6
Total.....	48.15	100.0

The same analysis is obtained when oxygen equivalent to net sulfur is first set aside from the oxygen in the coal and the net hydrogen is computed equivalent to the remaining oxygen. Thus, either method of calculation may be used, but it is preferable to follow the method chosen, since it conforms to the definition of net hydrogen as given on page 101.

If the sulfur in the ash be neglected, the following is obtained:

Basis: 100 lb coal.

	Pounds	Mols or atoms
C.....	57.22	4.77
H ₂	5.64	2.79
N ₂	1.41	
S.....	5.06	0.158
Ash.....	14.67	
O (by difference).....	16.00	1.00

Net H₂, $2.79 - 1.00 = 1.79$ mols

Net H₂, $1.79(2.02) = 3.62$ lb, or 3.62%

O₂ for theoretical combustion, $4.77 + 0.158 + 1.79/2 = 5.82$ mols

Excess O₂, $0.80(5.82) = 4.66$ mols

N₂ from air, $(5.82 + 4.66)(79/21) = 39.5$ mols

The error is about 6 per cent of the net hydrogen. However, the error made in the gas analysis is much less, because the net hydrogen requires only about 8% of the total oxygen used for combustion.

Flue-gas composition (dry, SO₂-free, S in ash neglected):

Gas	Mols	Per cent
CO ₂	4.77	9.75
O ₂	4.66	9.55
N ₂	39.5	80.7
Total.....	48.93	100.00

Comprehensive furnace tests. In order to summarize the ideas presented in Chaps. 2 and 3 and in this chapter, two examples will be given, in each of which a number of factors are brought together in one problem. This makes the apparent complexity of the problem greater, but in reality the individual computations merely employ step by step the principles already developed.

Because of the ready availability of complete and carefully obtained data, the examples chosen are from the field of power generation. Combustion of fuels under a boiler in a power plant is a relatively standardized operation, and thoroughgoing procedures for testing boiler furnaces have been published.¹ These procedures are a valuable guide to the chemical engineer, although he must frequently modify them in order to deal with the infinite variety of conditions under which fuels are burnt in chemical industry.

¹ ASME, "Power Test Codes," The Society, New York.

Illustration 4. The stack gas from a boiler furnace contains 10.8% CO_2 , 0.2% CO , 9.0% O_2 , and 80.0% N_2 . These gases enter the stack at 760°F , at a draft of 0.5 in. of water; 1200 lb of coal are burnt per hour. The proximate analysis of the coal as fired is 1.44% moisture, 34.61% volatile matter, 57.77% fixed carbon, and 6.18% ash, and the heating value is 14,350 Btu/lb. An analysis for carbon and sulfur shows these to be 78.76% and 0.78% respectively. Furthermore, it is known that coal from the same field averages 1.3% N. The volatile matter of the refuse (dry) is 4% and the fixed carbon 21%. Air in the boiler room has a temperature of 74°F , and is 65% saturated with water vapor. The barometer is 29.7 in. Compute

1. The per cent heat loss due to unburnt combustible
2. The per cent heat loss due to CO in the stack gas
3. The per cent of the heating value required to vaporize the total water vapor formed on combustion
4. The per cent heat loss as sensible heat in the stack gas
5. The per cent excess air used in the combustion
6. The cubic feet of air used per minute for combustion
7. The cubic feet of gas entering the stack per minute

Solution. It is obvious that the composition of the flue gas is determined not by total combustible fired, but only by combustible actually burnt. The data for securing the relation between the combustible fired and that burnt are found in the analyses of fuel and refuse. On the other hand, the analysis of the fuel is not complete, and hence the relation between net hydrogen and carbon must be determined from the flue-gas analysis, this applying, however, only to combustible actually burnt. Therefore, in solving this problem the first step is to get the relation between combustible burnt and combustible fired from the analyses of fuel and refuse; next, to secure from the flue-gas analysis the relation between net hydrogen and carbon in combustible burnt; and finally, by tying these two together, to compute the composition of the fuel. With the data thus organized and tabulated, solution of the various parts of the problem reduces itself to selecting and combining the specific quantities required in each case.

Since the coal contains only 0.78% sulfur, the presence of sulfur can be neglected in all computations except the calculation of the combined water in the coal, by difference.

Basis: 100 lb coal.

	<i>Pounds</i>
VCM (volatile combustible matter).....	34.61
FC (fixed carbon).....	57.77
Total combustible.....	92.38
Carbon.....	78.76
Ratio, C/total combustible, $78.76/92.38 = 0.853$	
Ratio, $\text{VCM}/(\text{VCM} + \text{FC})$, $34.61/92.38 = 0.375$	

Basis: 100 lb refuse.

	Pounds
Volatile matter.....	4
Fixed carbon.....	21
Total combustible.....	25
Ash.....	75
Total.....	100
Uncoked combustible, $4/0.375$	10.7
Coke = carbon, $25 - 10.7$	14.3
Carbon in uncoked combustible, $10.7(0.853)$	9.1
Total carbon.....	23.4

Basis: 100 mols dry stack gas.

Gas	Mols	Atoms C	Mols O ₂
CO ₂	10.8	10.8	10.8
CO.....	0.2	0.2	0.1
O ₂	9.0	9.0
N ₂	80.0		
Total.....	100.0	11.0	19.9 O ₂ accounted for
80.0(21/79).....			21.25 O ₂ from air
O ₂ unaccounted for by analysis.....			1.35 O ₂ disappearance

Net H₂ burnt to H₂O, $2(1.35) = 2.70$ mols = H₂O from combustion

Pounds net H₂ burnt, $2.70(2.02) = 5.45$

Pounds C burnt, $11.0(12) = 132$

Net H₂ burnt/C burnt = $5.45/132$.

Basis: 100 lb coal as fired.

	Pounds
C, total.....	78.76
C in refuse, $6.18(23.4/75)$	1.93
C in gas.....	76.83 = 6.40 atoms
C as uncoked coal in refuse, $6.18(9.1/75)$	0.75
C corresponding to net H ₂ in gas, $* 78.76 - 0.75$	78.01
Net H ₂ to H ₂ O in gas, $(5.45/132)76.83$	3.17 = 1.57 mols
Net H ₂ in refuse, $(0.75/78.01)3.17$	0.0305
Total net H ₂ in coal, $3.17 + 0.03$	3.20

Coal analysis

C.....	78.76
Net H ₂	3.20
S.....	0.78
N.....	1.30
Ash.....	6.18
Moisture.....	1.44 = 0.08 mol
Total.....	91.66
Combined H ₂ O.....	8.34
Total.....	100.00

Combined water in gas, $8.34(78.01/78.76)$ 8.26 = 0.46 mol

Total H₂O in gas from coal, $1.57 + 0.08 + 0.46$ 2.11 mols

* This is the total carbon in the coal from which came the net hydrogen in the gas.

These preliminary calculations give the complete analysis of the fuel and the distribution of the combustible matter between gas and refuse. One can now proceed to get answers to the specific questions of the problem.

1. *The per cent heat loss due to unburnt combustible.* The ash is the connecting link between coal and refuse.

Basis: 1 lb coal.

Heat loss as unburnt coal:

Lb ash	Lb uncoked combustible in refuse	Fraction loss	
0.0618	10.7	100	100
	75	92.38	$\frac{100}{92.38} = 0.95\%$

Heat loss as coke:

Lb ash	Lb coke in refuse	Chu	Btu	
0.0618	14.3	97,000	1.8	100
	75	12		14,350
$\frac{100}{14,350} = 1.19\%$				
Total heat loss = 1.19 + 0.95 = 2.14%.				

2. *The per cent heat loss due to CO in the stack gas.*

Atoms C in gas	Mols gas	Mols CO	Chu	Btu	
0.0640	100	0.002	68,300	1.8	$\frac{100}{14,350} = 1.0\%$ heat loss
	11.0	100			

3. *The per cent of the heating value required to vaporize the total water vapor formed on combustion.*

Mols H ₂ O from coal	Lb	Btu	
0.0211	18	1052	$\frac{100}{14,350} = 2.79\%$

4. *The per cent heat loss as sensible heat in the stack gas.* It is first necessary to obtain the total quantity of stack gas, *i.e.*, wet stack gas. The water in the combustion gases from a coal-fired furnace comes from two sources: the fuel, and the humidity in the air used for combustion. That from the fuel consists of original moisture, combined water, and that formed on combustion of the net hydrogen in the fuel. The total H₂O from the coal, including combustion of net H₂, has been calculated to be 2.11 mols per 100 lb coal, or $2.11(11.0/6.40) = 3.62$ mols per 100 mols of dry stack gas.

Water vapor from the air, 65% saturated at 74°F, with barometer at 29.7 in., is computed as follows:

Vapor pressure water at 74°F = 0.84 in.

Partial pressure of water in air, $0.65(0.84) = 0.54$ in.

Partial pressure of dry air, $29.7 - 0.54 = 29.16$ in.

Basis: 100 mols dry stack gas.

Mols N ₂	Mols dry air	
80.0	100	0.54
	79	29.16

= 1.88 mols H₂O from air

Total water vapor is $3.62 + 1.88 = 5.5$ mols.

The sensible heat of each component in the stack gas above 74°F equals the number of mols times the average heat capacity between 74 and 760°F times the temperature difference, $760 - 74$, or 686 Fahrenheit degrees. For all practical purposes, the average heat capacity based on 74°F is the same as that based on 60°F and can be read from Fig. 1-3.

Gas	Mols	$M\bar{c}_{p,av}^\circ$ from Fig. 1-3	Temp. change	Sensible-heat loss, Btu
CO ₂	10.8	10.5	686	78,000
CO }.....	80.2	7.1	686	392,000
N ₂ }				
O ₂	9.0	7.4	686	46,000
H ₂ O.....	5.5	8.4	686	32,000
Total.....	105.5	548,000

Basis: 1 lb coal.

Atoms C	Btu loss	
0.0640	548,000	100
	11.0	14,350

= 22.2% of heat of combustion

5. *The per cent excess air used in combustion.* This may be calculated from the gas analysis in the usual way.

$$\frac{(9.0 - 0.1)100}{21.25 - (9.0 - 0.1)} = 72\% \text{ excess air}$$

The above result, however, bases the excess air on the theoretical amount required only for the combustible that is actually burnt. While the result is nearly correct (only 2.14% of the heating value of the coal is lost as unburnt combustible), it is advisable to recompute the excess air on the basis of the coal analysis.

$$\begin{aligned}
 78.76/12 &= 6.56 \text{ O}_2 \text{ required for C} \\
 (3.20/2.02)/2 &= 0.79 \text{ O}_2 \text{ required for net H}_2 \\
 &= 7.35 \text{ O}_2 \text{ required for combustion} \\
 8.9(6.40/11.0) &= 5.18 \text{ O}_2 \text{ used in excess} \\
 (5.18/7.35)100 &= 70.5\% \text{ excess air}
 \end{aligned}$$

The figure of 70.5% is the one that should be reported.

If one has a complete coal analysis that is independent of the gas analysis, it is possible to get an independent check on the excess air as shown on page 49. In this case the coal analysis has been "built up" from the analyses of gas and refuse and is, therefore, not independent of them. Consequently, only one result is possible.

6. *The cubic feet of air used per minute for combustion.*

Lb coal	Atoms C in gas	Mols N ₂	Mols dry air	Mols humid air	Cu ft, s.c.	Cu ft, 29.7 in.	
1200	6.40	80.0	100	29.7	359	29.92	534
60	100	11.0	79	(29.7 - 0.54)		29.7	492

= 4710 cu ft/min

7. *Cubic feet of gas entering stack per minute.* A draft of 0.5 in. water is equal to $(0.5/13.6) = 0.04$ in. Hg. The pressure of the stack gas is, therefore, $29.7 - 0.04 = 29.66$ in. Hg.

Lb coal	Atoms C in gas	Mols wet gas	Cu ft, s.c.	Cu ft, 29.66 in.	
1200	6.40	105.5	359	29.92	1220
60	100	11.0		29.66	492

= 11,000 cu ft/min

Illustration 5. An exceptionally painstaking and thorough series of tests has been made on a twin boiler installation fired with pulverized coal, at Hell Gate Station in New York City.¹ The following is a selection from the mass of data reported and summarizes the analyses and flow rates observed during test No. 1 on boiler No. 91:

DATA

Duration of test.....	10 hr
Proximate analysis of dry fuel.....	22.46% VCM, 70.17% FC, 7.36% ash
Ultimate analysis of dry fuel.....	83.05% C, 4.45% H, 3.36% O, 1.08% N, 0.70% S, 7.36% ash
Heating value of dry fuel.....	14,581 Btu/lb
Moisture in fuel as fired.....	3.90%
Orsat analysis of gas sample withdrawn from the furnace.....	15.6% CO ₂ , 3.4% O ₂ , 0.0% CO, 81.0% N ₂
Orsat analysis of gas sample taken at the air-heater outlet.....	14.4% CO ₂ , 4.7% O ₂ , 0.0% CO, 80.9% N ₂

¹ W. E. Caldwell, *Trans. ASME*, **56**, 65 (1934).

Hourly quantities:

Fuel as fired.....	37,859 lb
Dry refuse.....	3113 lb

Air supply:

Humidity.....	0.0048 lb H ₂ O per pound dry air
Temperature.....	80°F

Analysis of dry refuse.....	14.0% combustible
-----------------------------	-------------------

Check the consistency of the data in as many ways as possible.

Solution. The data to be checked for consistency are essentially the analytical portions of the results of the test. The best test of reliability is to see if the figures agree with the law of conservation of chemical elements. Another way of assessing the dependability of the data is to compare the analytical results with empirical correlations, such as those of Calderwood and Dulong.

In the various streams entering and leaving the furnace, the four principal elements to be accounted for are carbon, hydrogen, oxygen, and nitrogen. According to the law of conservation of elements, the input of each of these elements, under conditions of steady operation, must equal the output. However, an immediate comparison of the data with the requirements of this law is not possible, because the only flow rates available are those of the fuel and refuse, and no information is given on the rate of air supply, the rate of production of dry flue gas, or the amount of moisture associated with the dry flue gas. The flow rates of these three streams—dry air, dry flue gas, and moisture—are unknown; hence three principles or relationships must be utilized to determine them before an element balance can be made. As a practical method of solving the problem, one may adopt the procedure of assuming that input and output are in balance for three of the major elements in the process and then checking to see if, on the basis chosen, the data show an equality between input and output of the fourth element. The results obtained by calculations of this sort depend on which three elements are chosen and thus reflect the matter of choice. However, in examples like the present one, it is customary to use a carbon balance to relate the fuel and refuse to the dry flue gas, to use an oxygen balance to determine the moisture in the flue gas, and to use a nitrogen balance to relate the dry flue gas to the air supply. When the quantities of the various streams have been established in this manner, the consistency of the experimental data can then be checked by seeing if the figures show an equality between input and output of hydrogen.

Table 4-1 summarizes the results of material-balance calculations based on 100 lb atoms of carbon in the dry furnace gas and using balances based on carbon, nitrogen, and oxygen to arrive at the various quantities. The combustible material in the refuse, assumed to be substantially all carbon, has been calculated from the measured quantity of refuse, rather than

from an ash balance. The further assumption has been made that all sulfur entering the furnace in the coal leaves in the gases in the form of sulfur dioxide and is included with the CO_2 .

Preliminary calculations.

C in fuel fired in 1 hr, 37,859(0.961)(0.8305).....	30,216 lb
C in refuse in 1 hr, 3113(0.140).....	436
C burnt in 1 hr, by difference.....	29,780 lb
Per cent of C in fuel burnt, (29,780/30,216) 100.....	98.56
Per cent of C in fuel left in refuse.....	1.44

Basis: 100 lb dry fuel.

	Pounds	Atoms or mols
C.....	83.05	6.92
C in refuse.....	0.10
C in gas.....	6.82
H_2	4.45	2.21
O.....	3.36	0.21
N_2	1.08	0.04
S.....	0.07	0.02
C + S in gas.....	6.84
Moisture, 100 (0.039/0.961)/18.....	0.225

Basis: 100 mols dry furnace gas.

Gas	Mols	Atoms C, S	Mols O_2	Mols N_2
CO_2, SO_2	15.6	15.6	15.6	
O_2	3.4	3.4	
N_2	81.0	81.0
Total.....	100.0	15.6	19.0	81.0

C in gas, (6.82/6.84) 15.6 = 15.56

S in gas, (0.02/6.84) 15.6 = 0.04

N_2 from coal, (0.04/6.84) 15.6 = 0.09

Inspection of Table 4-1 shows that input and output of H_2 agree within about 8%. In addition, the figures in the table serve to emphasize the fact that H_2 plays a relatively minor role in the total input and output, compared to C, O, and N_2 . When this is considered and it is recalled that all errors in sampling and analysis have been thrown on the H_2 tally, the agreement must be classed as good.

From the point of view of the combustion reactions, the method of accounting on H_2 may be open to criticism, in that a balance has been made on total H_2 , whereas the only portion that actually enters into the

reactions, in the sense of consuming O_2 from the air, is net H_2 . From the table, it is clear that net H_2^* in the fuel is $32.4 - 3.1 = 29.3$ mols, while net H_2 as derived from O disappearance is $277.0 - 244.4 = 32.6$ mols. On a basis of net H_2 instead of total H_2 , the discrepancy between input and output is approximately 10%. On either basis, the absolute difference between input and output of H_2 is the same. Therefore, an adequate picture of the consistency of the data could have been secured by a balance of net H_2 alone; and the balance on total H_2 could have been omitted.

TABLE 4-1. MATERIAL BALANCE CALCULATIONS (ILLUSTRATION 5)

Item	Mols or atoms				
	C	H_2	O	N_2	S
Input:					
Dry fuel.....	101.45	32.4	3.1	0.6	0.3
Moisture in fuel.....	3.3	3.3		
Dry air.....	277.0	520.4	
Moisture in air.....	5.1	5.1		
Total.....	101.45	40.8	288.5	521.0	0.3
Output:					
Dry furnace gas.....	100.00	244.4	521.0	0.3
Moisture in furnace gas....	44.1	44.1		
Refuse.....	1.45				
Total.....	101.45	44.1	288.5	521.0	0.3

As compared to the furnace-gas sample, the Orsat analysis on the sample taken at the air-heater outlet shows more O_2 and less CO_2 , with a slight drop in N_2 . The most probable explanation is a small leakage of air into the duct between the furnace and the outlet of the air heater, since this section of a furnace is normally under an appreciable draft and a relatively slight leakage of air will account qualitatively for the observed facts. Quantitatively, the situation can be analyzed by an over-all balance along the same lines as before, with the air leak included in the supply of air to the furnace. However, the two gas analyses are most easily compared by making a carbon balance and computing the net hydrogen in the air-heater outlet gas. If the two analyses are consistent, each should indicate the same ratio of net hydrogen to carbon. Furthermore, the leakage of O_2 and N_2 between the two sampling points can be calculated by means of balances on these elements, and the ratio of O_2 leakage to N_2 leakage should correspond to the analysis of air.

* This assumes that net H_2 is as defined on p. 101 and is the total H_2 minus that equivalent to available oxygen. The oxygen required for combustion is that necessary to combine with C, S, and the net H_2 as so defined.

If the Orsat analysis on the air-heater-outlet sample is corrected for the presence of SO_2 and converted to the same basis employed in preceding work, *i.e.*, 100 atoms of carbon in the gaseous products of combustion, it is found that the total atoms of O and mols of N_2 are 266.2 and 564.0, respectively. Input of O computed from the amount of N_2 and the composition of air is $(564.0)(21)(2)/(79) = 300.0$, and the value of net H_2 obtained from oxygen disappearance is $300.0 - 266.2 = 33.8$ mols. This figure checks quite well with the value of 32.6 mols derived from the furnace-gas analysis.

By difference between the two gas analyses, both on a basis of 100 atoms of carbon, the leakage of O_2 is $(266.2 - 244.2)/2 = 11.0$ mols, while the leakage of N_2 is $564.0 - 521.0 = 43.0$ mols. The per cent O_2 in the leakage is $(11.0)(100)/(11.0 + 43.0) = 20.7$. Agreement with the known composition of dry air is obviously close.

As noted previously, the observed weight of refuse, 3113 lb/hr, can be checked by means of an ash balance. The result is

$$(37,859)(0.961)(0.0736)/0.860 = 3120 \text{ lb/hr}$$

which represents substantial agreement.

It remains to compare the analytical data with the Calderwood and Dulong equations. As calculated from the former (page 104) the per cent carbon in the dry fuel equals

$$5.88 + 0.00512[14,581 - (40.5)(0.70)] \\ + 0.0053[80 - (100)(22.46)/70.17]^{1.55} = 82.61\%$$

By the latter formula (page 104), the heating value of the dry fuel is

$$14,544(0.8305) + 62,028(0.0445 - 0.0336/8) + 4050(0.007) \\ = 14,630 \text{ Btu/lb}$$

The directly measured values are 83.05% C and 14,581 Btu/lb; and in each case agreement is within the accuracy of the correlations.

One is justified in concluding that the data selected for examination are remarkably consistent and form a sound and trustworthy foundation on which to build a structure of material and energy balances describing the performance of the unit.

PROBLEMS

1. Examination of a Wyoming coal as received yields the following information: volatile matter, 31.4%; fixed carbon, 46.0%; ash, 3.1%; moisture, 19.5%; negligible sulfur; heating value, 10,100 Btu/lb. Estimate the per cent total carbon in the coal as received.

Ans. 56.6.

2. Study of a large number of samples of coal from the Connellsville, Pa., field indicates that the average analysis of the coal in this field is 27.5% volatile matter, 63.5% fixed carbon, 6.0% moisture, 3.0% ash, and negligible sulfur. The average heating value is 14,150 Btu/lb. A sample from a certain mine in the field is found to

contain 15% ash and 8% moisture. Estimate the per cent total carbon and the heating value of the coal thus sampled.

3. The following analyses on an "as received" basis are taken from E. S. Moore's "Coal":¹

Fuel	Per cent									Heating value, Btu/lb
	Mois- ture	V.M.	F.C.	Ash	S	H	C	N	O	
Lignite.....	34.55	35.34	22.91	7.20	1.10	6.60	42.40	0.57	42.13	7,090
Bituminous.....	3.24	27.13	62.52	7.11	0.95	5.24	78.00	1.28	7.47	13,919

(a) Using only the heating value and the proximate analysis, estimate the total carbon in each fuel. What is the per cent error in each case?

(b) Using the ultimate analysis, estimate the heating value of each fuel. What is the per cent error in each case?

4. A typical high-grade semibituminous coal has been found to contain 16.8% volatile matter and 83.2% fixed carbon on an ash- and moisture-free basis. On the same basis the heating value is 15,880 Btu/lb, and the sulfur content is 0.79%.

(a) Estimate the weight ratio of net hydrogen to carbon in the coal.

(b) Estimate the ultimate analysis of this coal on an ash- and moisture-free basis, on the assumption that the nitrogen content is 1.2%.

5. A billet-preheating furnace uses a coal containing 74.0% C, 4.8% H, 9.4% ash, and negligible S and N. This furnace is to be fired with 50% excess air.

(a) Calculate the flue-gas analysis on the assumption of complete combustion.

Ans. 12.5% CO₂, 7.1% O₂, 80.4% N₂.

(b) Repeat on the assumption that 10% of the carbon burns to CO only.

Ans. 11.25% CO₂, 1.25% CO, 7.7% O₂, 79.8% N₂.

6. A coal containing 70.1% C, 6.9% moisture, 8.0% ash, and negligible sulfur and nitrogen is burnt in a furnace under such conditions that the average Orsat analysis of the flue gas is 10.5% CO₂, 0.5% CO, and 8.6% O₂. The air enters the furnace at 80°F and is practically dry. The flue gas goes to the stack at 800°F, and the barometer is 740 mm. Calculate the following:

(a) Per cent net hydrogen in the coal as fired.

(b) Ultimate analysis of the fuel as fired.

(c) Per cent excess air used in combustion.

(d) Mols of air entering the furnace per pound of coal fired.

(e) Partial pressure of water vapor in the flue gas.

7. A boiler is fired with a coal containing 76.0% C and 8.1% ash, burnt under conditions such that elimination of combustible matter from the refuse is complete. The air enters the furnace at 90°F and is 80% saturated with water vapor at this temperature. The sulfur and nitrogen in the coal are negligible. The flue gases go to the stack at 1 atm and 640°F. The average flue-gas analysis shows 12.6% CO₂, 6.2% O₂, and 1.0% CO. Calculate the following:

(a) Per cent of net hydrogen in the coal.

(b) Per cent excess air used in the furnace.

(c) Ultimate analysis of the coal.

(d) Cubic feet of wet flue gases going to the stack per pound of coal fired.

(e) Cubic feet of wet air entering the furnace per pound of coal fired.

¹ John Wiley & Sons, Inc., New York, 1922.

8. A boiler is fired with powdered coal, known to be low in sulfur and carrying, as fired, 4.8% moisture and 10.0% ash. The barometer is 750 mm, the air temperature 92°F, and the partial pressure of water vapor in the air 20 mm. Combustible is well burnt out of the refuse. The firing rate is 3180 lb of coal per hour. Firing conditions are steady. Over an 8-hr period the average analysis of the stack gas is 14.26% CO₂, 0.52% CO, 0.41% H₂, 4.32% O₂, and 80.49% nitrogen and noble gases. The partial pressure of water vapor in the stack gas is found by the dew-point technique to average 68.8 mm, and the stack gas temperature is 444°F. Calculate the pounds of dry air used in this furnace per pound of coal as fired.

9. The laboratory reports the following ultimate analysis of a coal: 68.2% C, 6.2% H, 1.4% N, 3.0% S, 17.3% O, and 3.9% ash. Calculate the pounds of dry air required per pound of this coal (as analyzed) to furnish 20% excess air for its combustion, assuming that the original mineral fraction of the coal (before combustion) contains only traces of sulfur and that this element goes off in the gas as SO₂.

Subsequent examination of the coal shows that practically all the sulfur in it is present in the form of FeS₂. Recalculate the pounds of air per pound of coal in the light of this additional fact.

10. On an "as received" basis the proximate analysis of a representative coal from the Altoona Mine of Polk County, Iowa, is 13.9% moisture, 37.0% volatile matter, 35.2% fixed carbon, and 14.0% ash. On the same basis the ultimate analysis is 54.7% C, 5.5% H, 0.8% N, 6.2% S, and 18.8% O. The heating value is 10,244 Btu/lb. On the assumption that this coal is well burnt with 150% theoretical air, calculate the following quantities:

- Mols of air required per 100 lb of coal as fired.
- Orsat analysis of the flue gas.
- Mols of dry flue gas per 100 lb of coal.
- Dew point of the flue gas, if the barometer is 752 mm Hg and the entering air is practically dry.
- Cubic feet of wet flue gas leaving the stack per 100 lb of coal, if the stack gas temperature is 320°F.

11. A certain coal is pulverized and burnt under a boiler. The ultimate analysis of the coal on a dry basis is as follows: 72.1% C, 5.0% H, 1.5% N, 5.3% S, and 11.0% ash. The proximate analysis of the coal as received and fired is 3.4% moisture, 36.3% volatile matter, 49.6% fixed carbon, and 10.7% ash. On the same basis the sulfur is 5.1% and the heating value 12,720 Btu/lb. The sulfur is present in the coal largely as FeS₂. Firing conditions are such that all the iron may be assumed to burn to Fe₂O₃ and the sulfur to SO₂. The refuse is substantially free of combustible. A sample of the flue gas, collected and analyzed in an Orsat apparatus over mercury, contains 13.7% CO₂, 2.6% CO, 3.6% O₂, and 80.1% N₂.

(a) Assuming that only the Orsat analysis is known, calculate the atomic ratio of net hydrogen to carbon in the fuel and the per cent excess air used.

(b) Assuming that you are given the Orsat analysis as reported above and the proximate analysis, including sulfur and heating value, calculate the ultimate analysis of the coal on the dry basis.

(c) Recognizing that the Orsat analysis is incorrect because of sulfur and that there is nitrogen in the coal, correct the Orsat analysis, using the true ultimate analysis of the coal. In the corrected analysis list the percentages of CO₂, SO₂, CO, O₂, and N₂ from the air and that of N₂ from the fuel.

12. A coal containing 68.8% C, 10.1% ash, and 8.0% moisture is burnt in a stoker-fired furnace. The air used for combustion is 50% saturated with water at 70°F. The refuse is found to contain 13.1% combustible (essentially all carbon), 44.7% ash, and 42.2% moisture. The Orsat analysis of the flue gas is 9.8% CO₂, 10.5% O₂ and

no CO. Neglecting nitrogen and sulfur in the fuel, calculate the per cent excess air used.

13. In a test on a coal-fired furnace a representative sample of the coal as fired is found to contain 2.03% moisture, 14.47% volatile matter, 75.31% fixed carbon, 8.19% ash, and 2.26% S. The heating value of the coal as fired is 14,081 Btu/lb. The refuse contains 40.0% moisture, 15.3% fixed carbon, and 44.7% ash; and the flue-gas analysis is 13.0% CO₂, 1.1% CO, 1.6% H₂, and 5.6% O₂. Calculate the following:

(a) The per cent of the heating value of the fuel fired that is lost as unburnt carbon in the refuse.

(b) The ultimate analysis of the coal as fired. Neglect nitrogen in the coal.

14. The refuse from a coal-fired furnace is found to contain 36.0% moisture, 4.2% volatile matter, 13.6% fixed carbon, and 46.2% ash. The coal as fired contains 1.7% moisture, 29.2% volatile matter, 60.8% fixed carbon, and 8.3% ash, and has a heating value of 14,200 Btu/lb. Sulfur and nitrogen in the coal are negligible. The flue-gas temperature is 430°F. A recording CO₂ meter indicates that the average per cent CO₂ in the flue gas is 12.6 (dry basis). Under the firing conditions employed in this particular furnace, the CO and H₂ in the combustion gases are known to be very small in amount. The air used for combustion is 60% saturated with water vapor at 70°F. The barometer is normal. Estimate the following quantities as accurately as possible:

(a) Per cent of the heating value of the coal fired that is lost as unburnt combustible in the refuse.

(b) Complete Orsat analysis of the flue gas.

(c) Mols of water vapor in the flue gas per 100 mols of dry gas.

15. The coal received at a boiler house has an average heating value of 14,350 Btu/lb and the following average proximate analysis: 4% moisture, 23% volatile matter, 65% fixed carbon, 8% ash, and negligible sulfur and nitrogen. Before firing, the coal is wetted down to prevent dusting. The weight of water added for this purpose amounts to 10% of the weight of the coal as received at the boiler house. The cinder removed from the furnace contains on the average 8% volatile matter, 34% fixed carbon, and 58% ash. The air used for combustion enters at 60°F. The barometer is 740 mm Hg, and the partial pressure of water in the air is 12 mm. The stack gas leaves the furnace at 840°F, and an Orsat analysis of this gas, carefully conducted over mercury, shows 13.0% CO₂, 1.0% CO, 0.8% H₂, 5.9% O₂, and 79.3% N₂. Itemize the following heat losses as percentages of the heating value of the coal fired:

(a) Unburnt combustible in the cinders (higher heating value).

(b) Unburnt combustible in the stack gases (higher heating value).

(c) Latent heat of water in the stack gases.

(d) Sensible heat of the stack gases above 60°F.

16. A hand-fired boiler rated at 200 boiler horsepower (1 boiler hp = 33,475 Btu/hr) is being operated by three firemen, one man per 8-hr shift. The boiler is operated continuously at essentially rated load for an average of 7200 hr/year. The coal fired costs \$12/ton and has an average heating value of 14,280 Btu/lb. Its average ultimate analysis is 79.4% C, 5.7% H, 9.8% O, 0.7% S, 1.4% N, and 3.0% ash. The average temperature of the air and fuel is 70°F, and the partial pressure of water in the air is assumed to average 50% of saturation. The mean annual barometer is 748 mm Hg. Losses of heat from the furnace to the surroundings are approximately 5% of the heating value of the coal as fired.

If the dampers are adjusted correctly and the boiler is fired with care, it can be operated with 50% excess air in such a way as to achieve substantially complete combustion at all times. Under these conditions a stack temperature of 500°F can be maintained. However, a check reveals that the firemen are negligent in controlling the secondary air, with the result that the average excess air is 100% and the stack

gas temperature 550°F. Combustion is complete 95% of the time, but for 5% of the time, because of improper firing, the stack gas contains 0.5% CO, as shown by Orsat analysis.

In order to induce the firemen to exercise more care in operation, the management has agreed to give them a bonus of 20% of the fuel saving that they can realize by careful control of the combustion. Determine the yearly bonus that each fireman would receive if the boiler is operated so as to maintain 50% excess air and complete combustion at all times.

17. The following data on a boiler furnace represent average conditions over a week of steady operation. The furnace is fired with a coal the ultimate analysis of which is 68.36% C, 5.25% H, 0.82% S, 1.32% N, 10.50% O, and 13.75% ash. Its heating value is 12,400 Btu/lb. The dry refuse contains 11.58% unburnt combustible, essentially all carbon. All sulfur in the coal is gasified. Careful analysis of the flue gas over mercury shows 12.99% CO₂, 0.61% CO, 0.73% H₂, 5.81% O₂, and 79.86% N₂. The air temperature is 78°F, the barometer 754 mm Hg, and the partial pressure of water vapor in the air 18 mm Hg. The draft at the base of the stack at the point where the flue gas is sampled is 2.46 in. H₂O, the temperature of the gas is 434°F, and the partial pressure of water vapor in the flue gas at the base of the stack is 87 mm Hg. The temperature of the boiler feedwater is 71.3°F, and the boiler operates under a pressure of 618 psig, producing essentially saturated steam. Test this information for consistency in as many ways as possible, and state your opinion of its reliability.

18. An oil refinery cracks high-molecular-weight oil vapors by passing them through a large reactor containing a finely divided catalyst, which consists of a mixed silica-alumina gel. The reactor is operated at a temperature level of 1015°F. The gel contains a small amount of water, presumably chemically combined. At any rate it is held very stably at the temperature of the operation. The chemical reactions result in deposition on the catalyst of a considerable quantity of carbon, together with a certain amount of hydrocarbons. The latter are presumably held on the catalyst by adsorption. The catalyst also carries approximately 0.032% of iron on a combustible-free basis. The catalyst is withdrawn from the cracking vessel at uniform rate, is fed through a stripping zone where the hydrocarbons are removed from it so far as practicable by contact with steam, and then passes into a second vessel where the carbon is burnt off it with air. Because the catalyst is sensitive to heat, the temperature level in the second vessel is kept at approximately 1080°F. In this so-called regenerator the catalyst is suspended as a highly turbulent, high-density mass in the air flowing through it. The operation is remarkably uniform over periods of days.

Over a specific test period the carbon content of the spent, contaminated catalyst entering the regenerator is found by ultimate analysis to be 4.62%. The carbon content of the catalyst removed continuously from the regenerator and recycled to the cracking zone is 3.48%. The analysis of the combustion gases leaving the top of the regenerator is 10.4% CO₂, 8.6% CO, 0.8% O₂, and 80.2% N₂. At normal atmospheric pressure the dew point of the air supplied to the unit averages 80°F, and the dew point of the combustion gases averages 86°F.

The above data have been taken with care and checked repeatedly. They seem to be thoroughly dependable so far as they go. What do the figures mean to you?

Chapter 5

SECONDARY FUELS

Producer gas. As with furnaces and kilns, more information as to the performance of a gas producer can be secured by analysis of the gas than from any other single source. A complete test on a producer set is time-consuming, and the equipment is usually so arranged as to make it difficult or impossible to secure all the data needed, particularly the volumes of air used or of gas formed. These are hard to measure because of the large volumes involved, the variations in rate of production, and the expense and inconvenience of meters of sufficient size and precision to handle the gases. As in the case of ordinary furnace operations, the quantity of fuel used can, however, be easily and accurately determined. If its carbon content and that of the gas are known, a carbon balance, corrected for soot, tar, and any unburnt combustibles in the refuse, can be used to compute the quantity of gas. As will later appear, the corrections for soot and tar constitute the crux of the problem.

It is sometimes necessary to estimate rather than measure the quantity of steam consumed by the unit, and it is always desirable to determine the degree of decomposition of steam in the producer. One can get valuable information on both these points through hydrogen and oxygen balances, based on analysis of the gas and experimental determination of its water content, by allowing for water vapor in the air and for moisture and combined water in the fuel.

Gas-producer computations are unique in that the manufacture of producer gas represents the combination of primary combustion with water-gas formation. A large fraction of the volatile matter of the fuel remains in the gas as CO, hydrocarbons, and hydrogen. Hydrogen and oxygen (the latter combined as CO or CO₂) are also introduced into the gas by decomposition of the steam injected or of some of the combined water in the fuel. As in combustion in furnaces, the gas analysis of itself can be made to yield important quantitative information as to these reactions.

Illustration 1. The average analysis of a certain producer gas is

	<i>Per cent</i>
CO ₂	9.84
O ₂	0.04
C ₂ H ₄	0.18
CO.....	18.28
H ₂	12.90
CH ₄	3.12
N ₂	55.64
Total.....	100.00

What conclusions may be drawn from these figures alone?

Discussion. As in combustion calculations, the figures are first tabulated so that the quantities of the individual elements are shown, taking as a basis 100 mols of dry gas. Assuming that all the nitrogen comes from the air used, the corresponding oxygen is next computed. This is less than the total oxygen present in the gas (note the difference from ordinary combustion calculations), the remainder of necessity being equivalent to water decomposed, since this is the only other possible source of oxygen. The mols of water decomposed and the hydrogen formed therefrom are obviously twice the corresponding mols of oxygen. The hydrogen from the steam is, in turn, less than the total present; the difference between the two must be the net hydrogen from the fuel. All these calculations are indicated in the following table.

Basis: 100 mols of dry producer gas.

Gas	Mols	Atoms C	Mols H ₂	Mols O ₂
CO ₂	9.84	9.84	9.84
O ₂	0.04	0.04
C ₂ H ₄	0.18	0.36	0.36	
CO.....	18.28	18.28	9.14
H ₂	12.90	12.90	
CH ₄	3.12	3.12	6.24	
N ₂	55.64			
Total.....	100.00	31.60	19.50	19.02
O ₂ from air, 55.64(21/79).....				14.80
O ₂ from decomposition of water.....				4.22
H ₂ from decomposition of water, 4.22(2).....				8.44
H ₂ from net H ₂ in fuel.....				11.06

It will be noted that the oxygen in the gas comes from two separate sources, air and decomposition of water. By a nitrogen balance, that

from the former source is earmarked and set aside, that from the latter being obtained by difference. This makes it possible to earmark similarly that fraction of the total hydrogen derived from water, since it must be equivalent to the oxygen from the same source. The remainder of the hydrogen must come from the fuel.

The pounds of carbon per 100 mols of dry gas and the weight of net hydrogen and water decomposed on the same basis can be found.

	Pounds
C in gas, 31.60(12).....	379.2
Net H ₂ in gas, 11.06(2.02).....	22.3
H ₂ O decomposed, 8.44(18).....	151.8

From these figures several ratios can be obtained that are informative. For example, per pound of carbon gasified there are:

$$\begin{aligned}
 151.8/379.2 &= 0.400 \text{ lb H}_2\text{O decomposed} \\
 (100/379.2)359 &= 94.8 \text{ cu ft gas, d.s.c., produced} \\
 (55.64/379.2)(100/79)359 &= 66.8 \text{ cu ft air, d.s.c., used}
 \end{aligned}$$

It is usual to assume that the water decomposed thus calculated is limited to that entering as steam with the air, but such probably is not the case. It is true that in an updraft producer the moisture in the coal is driven off and swept out of the producer at a temperature too low to react with carbon at an appreciable rate. On the other hand, oxygen in the coal substance which is present as "combined water" does not come off upon thermal decomposition solely as water, but partly as CO, CO₂, and perhaps to some degree as oxygen-containing organic compounds. The latter almost certainly decompose into simpler molecules before leaving the producer. Consideration will show, however, that in so far as oxygen of the fuel reacts thus directly to yield CO and CO₂, an *equivalent* amount of hydrogen must be liberated so that *stoichiometrically* the result is the same as though the "combined water" of the fuel had first been set free as such and had then reacted with carbon. The data throw no light on the mechanism of these reactions, but fortunately it is entirely immaterial in the over-all performance of the producer. Similarly, of the net hydrogen in the coal some may burn to water and some may distill off as hydrocarbons, but the exact equivalent of all of it must appear in some form in the gaseous product. The computations correctly represent the over-all result, though the reaction mechanism may differ from that assumed in making them.

Interrelation of gas and fuel. If a producer is fired with a low-volatile fuel, such as coke or anthracite, the quantities of fuel and gas can be related by means of balances on carbon, of the type illustrated in

preceding chapters. On the other hand, high-volatile coals are often employed, and in such a case a satisfactory balance on carbon is made difficult by the complications due to formation of tar. In all updraft producers the thermal decomposition and distillation of the coal take place at high temperature in an atmosphere free of oxygen. In consequence, the cracking of the distillation products results in the formation of considerable quantities of tar and soot. Where the hot gas goes directly into a furnace beside the producer, substantially all the tar is carried into the furnace, but where the gas is piped any considerable distance, or cooled, the tar settles in the flues, separates out in the coolers, collects in the traps, and develops a general nuisance. Because of these conditions it is impossible to determine tar formation with any precision in a test run of normal duration.

Two alternative methods of meeting the problem are available. The first of these takes advantage of the fact that in a gas producer there is usually a stream of material not normally present in operating an ordinary furnace, namely, the steam used for the water-gas reaction in the producer. Moreover, the quantity or flow rate of this steam is usually easy to measure accurately. Therefore, it can be used as the basis of a balance for indirect determination of the amount of gas flowing. The second alternative is to find a method of estimating the quantity and composition of the tar produced in the operation of the unit, even though the direct determination of this tar be impossible. These two methods of solving the problem will be taken up in turn.

The steam supplied to the producer brings in hydrogen and oxygen, and theoretically one can use a balance based on either of these elements to tie the steam-supply rate into the gas-production rate. An oxygen balance is preferable because of the fact that the oxygen content of the tar is usually small enough to be neglected in an over-all balance. The method suffers from the fact that so much of the oxygen in the final gas comes from the air. Consequently, the oxygen from the steam must be determined by difference. Hence, unless it is an appreciable fraction of the total oxygen, its determination in the gas is inaccurate. This means that for the method to be dependable the steam/fuel ratio must be reasonably high. It also requires careful measurement of the moisture content of the gas produced, either by sampling for analysis before any moisture condensation due to cooling occurs, or by determination of the quantity or rate of condensation, together with analysis of the moisture content of the uncondensed residual gas. Despite these limitations, the method can on occasion be a valuable auxiliary technique in the determination of plant performance.

Illustration 2. A gas producer is being fired with a coal the ultimate

analysis of which on a dry basis is 78.5% C, 5.4% H, 1.4% N, 0.8% S, and 3.5% ash, and the corresponding volatile combustible matter, 36.2%. The heating value is 13,880 Btu/lb. As fired it contains 4.5% moisture. During the 63.3 hr of the test, 174,500 lb of coal were fired and 6770 lb of ash and clinker withdrawn, containing 14.2% combustible matter (practically all carbon). The gas analysis, carefully conducted over mercury, averaged 13.25% CO₂, 16.10% CO, 22.65% H₂, 3.50% CH₄, and 44.50% N₂ and inerts. Barometer averaged 766 mm Hg; air temperature, 23°C; and partial pressure of water vapor in it, 12 mm. The steam supplied to the blast was at 20 psig and 184°C. It was metered and totaled 256,000 lb during the test. The blast pressure was 5.35 in. water. The gas left the producer at 820°C, at practically atmospheric pressure, with a dew point of 65.5°C, corresponding to a vapor pressure of water of 192 mm. Practically all the sulfur in the coal showed up in the gas as H₂S. Calculate the cubic feet (d.s.c.) of gas produced per pound of coal as fired.

Solution. The fact that the fuel contains 36.2% volatile combustible matter indicates that the amount of tar is probably appreciable, and it is unwise to attempt a carbon balance in the absence of data on the quantity of tar and soot produced. An oxygen balance is required.

In problems of this type, it is usually easiest to begin with the gas analysis. However, in this case the gas analysis is not known completely until a preliminary correction is made for the effect of H₂S. A satisfactory approximation is to assume that the ratio of H₂S to total carbon in the gas is the same as the ratio of sulfur in the fuel to carbon in the fuel less carbon in the refuse. While this assumption is not exactly true, it does not introduce a significant error in the over-all results.

As a basis, choose 100 lb of dry fuel. On this basis the carbon in the refuse can be calculated either by an ash balance or from the measured quantity of ash and clinker. By the first method, the figure obtained is $3.5(14.2/85.8)$, or 0.580 lb. The second yields the result $6770(100)(0.142)/(0.955)(174,500)$, or 0.577 lb. By difference, carbon in the gas, tar, and soot is $78.5 - 0.6 = 77.9$ lb, or 6.49 atoms. Since sulfur in the fuel is $0.8/32$, or 0.025 atom, the desired ratio of sulfur to carbon is $0.025/6.49$, or 0.0039.

Now turn to the producer gas, choosing a basis of 100 mols of dry gas. Inasmuch as H₂S was absorbed in alkali and evidently reported as CO₂, the total atoms of C and S in the gas amount to $13.25 + 16.10 + 3.50$, or 32.85 atoms. From the ratio derived in the preceding paragraph, the portion of the gas consisting of H₂S is $32.85(0.0039/1.0039) = 0.13$ mol. By difference, CO₂ is $13.25 - 0.13 = 13.12$ mols. A complete tabulation of the gas analysis is now possible.

Gas	Mols	Atoms C	Mols H ₂	Atoms O
H ₂ S.....	0.13	0.13	
CO ₂	13.12	13.12	26.24
CO.....	16.10	16.10	16.10
H ₂	22.65	22.65	
CH ₄	3.50	3.50	7.00	
N ₂	44.50			
Total.....	100.00	32.72	29.78	42.34

The nitrogen from the fuel can be neglected with very little error, and the oxygen from the air determined by a nitrogen balance.

$$44.50(42/79) = 23.65 \text{ atoms O from dry air}$$

Similarly, a nitrogen balance can be used to find the oxygen input in the form of water vapor in the air.

$$44.50(100/79)(12)/(766 - 12) = 0.90 \text{ mol H}_2\text{O in air}$$

Oxygen in the producer gas as water vapor is obtainable from the measured dew point.

$$100[192/(766 - 192)] = 33.45 \text{ mols H}_2\text{O in gas}$$

On a basis of 100 mols of dry gas, one now knows the oxygen content of all streams for which one does not have directly measured flow rates and analyses and which contain significant amounts of oxygen. Hence, it is now possible to return to a fuel basis and set up an oxygen balance in which the only unknown is the volume of dry producer gas.

Choose a basis of 100 lb of dry coal, as before. By subtraction of the other constituents from 100, the oxygen content is found to be 10.4%.

$$10.4/16 = 0.650 \text{ atom O in dry coal}$$

$$100(4.5/95.5)/18 = 0.262 \text{ mol H}_2\text{O as moisture in coal}$$

$$100(256,000)/(0.955)(174,500)18 = 8.550 \text{ mols steam}$$

Let x = mols of dry gas produced. Set up an oxygen balance, as follows:

$$\begin{aligned}
 \left[\begin{array}{c} \text{Oxygen} \\ \text{in dry} \\ \text{coal} \end{array} \right] &+ \left[\begin{array}{c} \text{oxygen in} \\ \text{moisture} \\ \text{in coal} \end{array} \right] &+ \left[\begin{array}{c} \text{oxygen in} \\ \text{dry air} \end{array} \right] &+ \left[\begin{array}{c} \text{oxygen in} \\ \text{moisture} \\ \text{in air} \end{array} \right] &+ \left[\begin{array}{c} \text{oxygen} \\ \text{in} \\ \text{steam} \end{array} \right] \\
 0.650 &+ 0.262 &+ 0.2365x &+ 0.0090x &+ 8.550 \\
 &&&&= \left[\begin{array}{c} \text{oxygen} \\ \text{in dry} \\ \text{gas} \end{array} \right] &+ \left[\begin{array}{c} \text{oxygen in} \\ \text{moisture} \\ \text{in gas} \end{array} \right] \\
 &&&&= 0.4234x &+ 0.3345x
 \end{aligned}$$

Solving, $x = 18.5$ mols. The result is easily converted to cubic feet on a basis of coal as fired:

$$18.5(0.955)(359)/(100)$$

= 63.5 cu ft (d.s.c.) of gas produced per pound of coal fired

It is of interest to use the gas production determined by oxygen balance to check the carbon balance. On a basis of 100 lb of dry fuel, the carbon in the gas is $(18.5)(0.3272)(12) = 72.6$ lb, which compares with the figure of 77.9 lb corresponding to carbon in the fuel less that in the refuse. The difference, roughly 7% of the carbon in the fuel, evidently went to tar and soot.

It is also informative to check the hydrogen balance. This is conveniently done on a basis of 100 lb of dry coal, as follows:

H₂ input:

	<i>Mols</i>
Dry coal, 5.4/2.....	2.7
Moisture in coal.....	0.26
Moisture in air.....	0.17
Steam.....	8.55
Total.....	11.68

H₂ output:

Dry gas, (18.5)(0.2978).....	5.50
Moisture in gas, (18.5)(0.3345).....	6.20
Total.....	11.70

The calculations show that the output of H₂ exceeds the input by 0.02 mol. This of course cannot be true in actual fact and must be attributed to slight inaccuracies in the original data or calculations. Indeed this discrepancy is far less than one would anticipate from the probable accuracy of the measured data; *i.e.*, such a good check is fortuitous. It is evident nonetheless that in this particular case the amount of hydrogen contained in the tar and soot is very small, and a hydrogen balance would have led to substantially the same result as the one on oxygen. However, it is by no means safe to generalize from this instance and assume that one can always neglect the hydrogen content of tar. Indeed, the fact that tar always contains hydrogen is ground for the conviction that the close check was due to minor errors in the data.

It should be clear that if one attempts to evaluate the gas-flow rates in a producer by measuring the steam-flow rate, together with the other necessary analytical data, under operating conditions in which the rate of steam utilization is small relative to the gas quantities involved, precision will be sacrificed because one is dealing with small differences between large quantities. On the other hand, producers not infrequently operate with low steam rates. Indeed, conditions are encountered in which any other method of operation would involve serious sacrifice of thermal efficiency. It is obvious that one should have another method of estimating gas-flow rates.

The evidence indicates that the tar formation per pound of coal gasified

remains substantially constant for a given coal in a given equipment as long as operating conditions are not too widely varied. A satisfactory method of allowing for tar is, therefore, to secure data on tar formation over long periods of time and to use these figures in computing the results of a test rather than using the data on the tar obtained during the test itself. Since under normal conditions a large fraction of the tar separates out emulsified with water, it is imperative to have an analysis of the water content of the tar.

To get carbon and hydrogen balances on the producer, one must have the ultimate analysis of the tar. On the other hand, while tar formation is in no wise negligible, it is always a minor factor compared with the total combustible in the fuel, so that no serious error is introduced if its composition is estimated, particularly since it is known to be rich in carbon. In the absence of direct analyses of the tar in question, the authors usually assume it to contain 90% carbon and the rest hydrogen, although it is well recognized that it does carry some oxygen, nitrogen, and sulfur.

Illustration 3. The following data were obtained from a test on a Morgan gas producer. The feed was automatic, ensuring uniform rate of fuel supply and eliminating any serious variations in rate of gas production. Using the same kind of coal under similar conditions of operation over long periods of time, it has been found that the weight of dry tar produced is 3.9% of the weight of the coal fired. It is desired to determine the gas production, the steam decomposition, and a heat balance on the producer itself.

ABSTRACT OF TEST SHEET

		Per cent
Duration of run, hr.....	2.33	Combustible in refuse..... 9.99
Steam, lb/hr.....	338	
Steam pressure, psig.....	15	Coal analysis, wet basis:
Coal, lb/hr.....	866	Moisture..... 1.06
Temperature of air, °F:		C..... 69.40
Dry bulb.....	65.5	H..... 4.76
Wet bulb.....	59.4	S..... 1.48
Barometer, in. Hg.....	29.43	N..... 1.48
Temperature of exit gas, °F.....	1305	O..... 9.18
		Ash..... 12.64
Average gas analysis, per cent by volume:		
CO ₂	7.23	
III(C ₂ H ₄).....	0.58	
O ₂	0.38	Higher heating value of
CO.....	20.76	dry coal, 12,520 Btu/lb
H ₂	11.36	
CH ₄	2.98	
N ₂	56.71	

Determination of the water content of the gas was made in the following manner: A sample was drawn through a steam-jacketed filter of glass wool to remove tar and dust, and thence through an absorption bulb containing P_2O_5 . In this manner 14.40 liters of the dried gas were collected at $32.0^\circ C$ and at 759 mm pressure. The increase in the weight of the bulb was 0.8451 g.

Solution. The coal and gas analyses are tabulated, and by using the information regarding the refuse and tar, the distribution of carbon and hydrogen is shown.

Basis: 100 lb of coal as fired.

	Pounds	Mols or atoms
Moisture.....	1.06	0.06
C.....	69.40	5.78
H ₂	4.76	2.36
S.....	1.48	
N ₂	1.48	
O ₂	9.18	0.29
Ash.....	12.64	
Net H ₂ , 2.36 - 2(0.29).....		1.78
Combined water, 2(0.29).....		0.58
C in refuse, 12.64(9.99/90.01).....	1.40	0.12
C in tar, 3.9(0.9).....	3.51	0.29
C in gas, 5.78 - 0.12 - 0.29.....		5.37
Net H ₂ in tar, 3.9(0.10).....	0.39	0.19
Net H ₂ in gas, 1.78 - 0.19.....		1.59

Basis: 100 mols of dry gas.

Gas	Mols	Atoms C	Mols H ₂	Mols O ₂
CO ₂	7.23	7.23	7.23
Ill. (C ₂ H ₄).....	0.58	1.16	1.16	
O ₂	0.38	0.38
CO.....	20.76	20.76	10.38
H ₂	11.36	11.36	
CH ₄	2.98	2.98	5.96	
N ₂	56.71			
Total.....	100.00	32.13	18.48	17.99

These two tabulated analyses of the coal and gas show, each on its own basis, how much carbon is present in the gas. Using the amount of coal fired as given in the table of test data, the gas production can be estimated directly by a carbon balance.

Lb coal per hour	Atoms C in gas	Mols dry gas	
866	5.37	100	359
	100	32.13	

$$\frac{359}{32.13} = 52,000 \text{ cu ft d.s.c. per hour}$$

A diagrammatic representation of this problem is seen in Fig. 5-1.

A virtually independent check on the gas production may be had by using a hydrogen balance. Hydrogen occurs in so many places that it is best to tabulate the separate items.

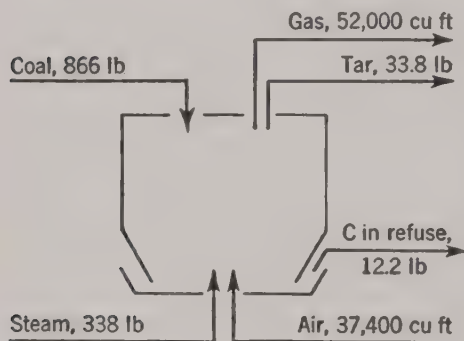


FIG. 5-1. Material balance on gas producer. Basis: 1 hr.

Hydrogen Input. Basis: 1 hr.

1. *From the coal.*

Moisture + combined water + net $H_2 = 0.06 + 0.58 + 1.59 = 2.23$ mols per 100 lb coal fired.

$$(2.23/100)866 = 19.3 \text{ mols/hr}$$

2. *From the steam.*

$$338/18 = 18.78 \text{ mols/hr}$$

3. *From the air.* This is obtained through the nitrogen in the producer

gas, from which the air used can be computed. Let the quantity of dry producer gas be x mols/hr. From the wet- and dry-bulb temperatures of the air, the humidity is 70 per cent (Fig. A-3). The vapor pressure of water at $65.5^\circ F$ is 0.63 in. This gives as the partial pressure of the water $0.70(0.63) = 0.44$ in. Hg, and as the pressure of the dry air $29.43 - 0.44 = 29.0$ in. Thus the hydrogen brought in by the air as water vapor is

Mols of producer gas	Mols N_2	Mols dry air	
x	56.71	100	0.44
	100	79	29.0

$$\frac{0.44}{29.0} = 0.0109x \text{ mols } H_2O \text{ vapor}$$

Hydrogen Output. 1. *As water vapor in gas.* The analytical data show that for every 14.40 liters of dry gas at $32.0^\circ C$ and 759 mm, there are 0.8451 g of water vapor.

Liters dry gas	At $0^\circ C$	At s.c.	
14.40	273	759	
	305	760	22.4

$$\frac{0.8451}{22.4} = 0.0377 \text{ g mol dry gas}$$

$$0.8451/18 = 0.047 \text{ g mol water}$$

$$0.047/0.575 = 0.0817 \text{ g mol of water per gram mol of dry gas}$$

This ratio is, of course, identical with the ratio, pound mols of water per pound mol of dry gas. Therefore, the hydrogen output in this form is $0.0817x$.

2. As H_2 in gas, $0.1848x$ mols.

The hydrogen balance is obtained by equating the input and output as calculated above.

$$19.3 + 18.78 + 0.0109x = 0.0817x + 0.1848x$$

Solving, $x = 149.0$, or $149.0(359) = 53,500$ cu ft, s.c., per hour.

The good agreement between this figure and that obtained from a carbon balance (52,000 cu ft) furnishes a check on the dependability of the data and the accuracy of the assumptions.

Steam Decomposition. This also may be calculated by either a carbon or a hydrogen balance. The steam actually used is 18.78 mols/hr. The steam decomposed is equal to the number of mols of hydrogen in the gas minus the net hydrogen from the coal.

1. *By carbon balance.*

Lb coal	Atoms C in gas	
866	5.37	18.48
	100	32.13

$$= 26.70 \text{ mols } H_2 \text{ in gas}$$

$$866(1.59/100) = 13.77 \text{ mols net } H_2 \text{ from coal}$$

$$12.93 \text{ mols } H_2 \text{ from steam}$$

$$(12.93/18.78)100 = 69\% \text{ decomposed}$$

2. *By hydrogen balance.*

$$149(18.48/100) = 27.60 \text{ mols } H_2 \text{ in gas}$$

$$13.77 \text{ mols net } H_2 \text{ from coal}$$

$$13.83 \text{ mols } H_2 \text{ from steam}$$

$$(13.83/18.78)100 = 76\% \text{ decomposed}$$

Energy Balance. The temperature of the surroundings ($65.5^\circ F$) will be taken as the reference point for all items of heat input and output, and all final results will be expressed on an hourly basis. The heat content (enthalpy) of water at the base temperature will be taken as zero in the liquid state.

Energy Input. The three sources of energy entering the system are (1) coal, (2) steam, and (3) air.

1. *Coal.* The heating value is given for dry coal; hence, the weight of dry coal must be used in computing the energy input from this source: $866(0.9894)(12,520) = 10,720,000$ Btu.

2. *Steam.* A pressure of 15 psig corresponds to

$$15(29.92/14.7) + 29.43 = 59.96 \text{ in. Hg}$$

To have this pressure, the steam (assumed saturated) must have a temperature of 249°F. The 338 lb of steam used per hour bring a quantity of heat into the system equal to the enthalpy of the steam at 249°F, less that of the liquid at 65.5°F, *i.e.*,

$$338(1163.7 - 33.6) = 382,000 \text{ Btu}^*$$

3. *Air.* Although the air used is at the reference temperature and hence brings in no sensible heat, the latent heat of its moisture content is a justifiable addition, although admittedly small in this case. Water in air used (calculated from the carbon balance result) is 28.45 lb, equivalent to $28.45(1057) = 30,000 \text{ Btu.}^\dagger$

Energy Output. Since the higher heating value of the fuel can be realized only when all water formed in combustion is condensed, and since the latent heat of all water entering the system in the vapor state has been considered as input, then the latent heat of all uncondensed water leaving the system will be an item in the energy output.

1. *Latent heat of water in gas.*

Basis: 1 hr.

Lb coal per hour	Atoms C in gas	Mols H ₂ O in gas	Lb H ₂ O	Btu
866	5.37	8.17	18	1057
	100	32.13		

= 225,000 Btu as latent heat of H₂O in gas

2. *Sensible heat in gas.* With small error, one can assume that the average specific heat of each gas between the temperature limits of 1305°F and 65.5°F is the same as the average specific heat between 1305°F and 60°F, read from Fig. 1-3. For each gas, the sensible-heat content equals the product of the number of mols, the average molal heat capacity, and the temperature difference, 1305 - 65.5, or 1239.5 Fahrenheit degrees. In view of the small amount of illuminants, the calculations may be simplified by counting the illuminants as CH₄.

* See Table A-3 in Appendix.

† The latent heat at 65.5°F is used, since water is included with other gases in computing sensible heat.

Basis: 1 mol dry gas.

Gas	Mols	$Mc_{p,av}^{\circ}$ from Fig. 1-3	Sensible- heat content, Btu
CO ₂	0.0723	11.3	1,011
O ₂	0.0038	7.7	36
CO.....	0.2076	7.4	1,900
H ₂	0.1136	7.0	985
N ₂	0.5671	7.3	5,130
CH ₄ + Ill.....	0.0356	13.2	581
H ₂ O.....	0.0817	8.8	890
Total.....	1.0817	10,533

The heat retained by the hot gases is

Lb coal per hour	Atoms C in gas	Mols dry gas	
866	5.37	100	$\frac{10,533}{32.13} = 1,526,000 \text{ Btu}$
	100	32.13	

3. Heat of combustion of the gas.

Basis: 1 mol of dry gas.

	Mols	Higher heating value, Chu	Chemical energy, Chu
Ill. (C ₂ H ₄).....	0.0058	337,000	1,960
CO.....	0.2076	67,600	14,030
H ₂	0.1136	68,300	7,750
CH ₄	0.0298	213,000	6,350
Higher heating value, per mol.....	30,090

Basis: 1 hr.

Lb coal per hour	Atoms C in gas	Mols dry gas	Chu	
866	5.37	100	30,090	$\frac{1.8}{32.13} = 7,850,000 \text{ Btu}$
	100	32.13		

4. Heat in tar. Assume that the heat of combustion of tar is equal to that of the component elements and that its specific heat is 0.5.

Heat of combustion:	Btu
866(0.039)(0.10/2.02)(68,300)(1.8).....	207,000
866(0.039)(0.90/12)(97,000)(1.8).....	442,000
	649,000
Sensible heat:	
866(0.039)(1,305 - 65.5)(0.5).....	21,000
Total heat in tar.....	670,000

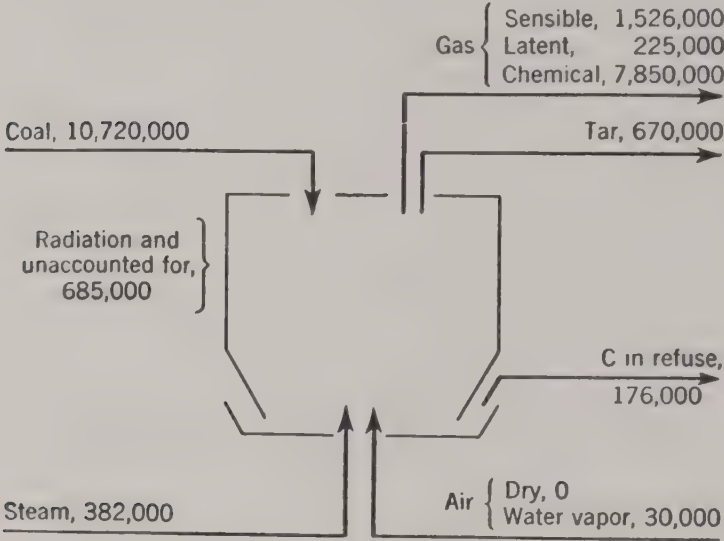


FIG. 5-2. Energy balance on gas producer. Figures represent Btu. Basis: 1 hr.

5. Heat of combustion of carbon in refuse.

Pounds coal per hour	Pounds C	Atoms C	Chu	
866	1.40		97,000	1.8
	100	12		

= 176,000 Btu

The energy balance may now be written (see also Fig. 5-2):

Energy input:	Btu
a. Coal (higher heating value).....	10,720,000
b. Steam (total heat - heat of liquid at 65.5°F).....	382,000
c. Latent heat at 65.5°F of atmospheric moisture.....	30,000
Total.....	11,132,000
Energy output:	
a. Latent heat of water in gas.....	225,000
b. Sensible heat of hot gases.....	1,526,000
c. Heat of combustion of gases.....	7,850,000
d. Total heat in tar.....	670,000
e. Heat of combustion of C in refuse.....	176,000
f. Radiation and unaccounted-for losses (by difference).....	685,000
Total.....	11,132,000

One of the most important engineering functions of material and

element balances is in the cross checking of experimental data as one means of evaluating their dependability. The following problems offer further constructive illustration of this point.

Illustration 4. The following is a partial summary of operating data on the performance of a set of gas producers of the Rochester Gas and Electric Corporation.¹

Fuel: Coke analyzing 0.6% moisture, 4.0% volatile combustible matter, 76.0% fixed carbon, and 19.4% ash, with a heating value of 11,900 Btu/lb. It was fired at the rate of 35 lb of dry fuel per square foot of grate area per hour and contained as fired 9.6% moisture.

Air: The consumption of air was 46.5 cu ft per pound of dry fuel, and its average temperature was 60°F.

Steam: The steam supplied to the blast was metered and found to be 0.53 lb per pound of dry fuel fired.

Blast: The pressure under the grate averaged 21.5 in. water; and the dew point of the blast at this same point was 142°F.

Gas: 7.1% CO₂, 0.3% O₂, 27.1% CO, 13.4% H₂, 0.4% CH₄, and 51.7% N₂. The volume of the producer gas was 71.4 cu ft per pound of dry fuel. The differential between the pressure under the grate and the gas leaving the producer averaged 19.5 in. water, and the dew point of this gas was 100°F.

Cinder: 14.0% combustible, 86.0% ash.

It can be assumed that the barometer was normal, that gas and air volumes were reported at 60°F and 30 in. Hg abs, saturated with water vapor, and that dew point measurements were made at atmospheric pressure. It is estimated that the relative humidity of the air was 80%.

As a check on the consistency of the data, compute the ratio of mols of water vapor to mols of nitrogen in the blast, at the point where it enters the fuel bed, by three independent methods, using in each method none of the above items of information used in either of the other methods, except the barometric pressure.

Solution. As the first step check the gas analysis in the usual way to see what information can be obtained from it alone.

Basis: 100 mols of dry producer gas.

	Mols	Atoms or mols		
		C	H ₂	O
CO ₂	7.1	7.1	14.2
O ₂	0.3	0.6
CO.....	27.1	27.1	27.1
H ₂	13.4	13.4	
CH ₄	0.4	0.4	0.8	
N ₂	51.7			
Total.....	100.0	34.6	14.2	41.9

¹ *Am. Gas Assoc. Proc.*, 1927, p. 1224; see also 1926, p. 1051.

Assuming a negligible amount of nitrogen in the fuel, one can use a nitrogen balance to determine the oxygen supplied by the air.

$$51.7(2)(21/79) = 27.5 \text{ atoms O from air}$$

$$41.9 - 27.5 = 14.4 \text{ atoms O} \approx 14.4 \text{ mols H}_2 \text{ from decomposed H}_2\text{O}$$

Thus, the figures show that net H₂ gasified from the fuel is 14.2 — 14.4, or —0.2 mol. It is, of course, impossible that the net H₂ in the coke should be negative; the fact that one obtains a small negative value, the magnitude of which is within the precision of an Orsat apparatus, must mean that the net H₂ in the coke employed as fuel in the Rochester producers is too small to be detected by the Orsat method of analysis, and the combustible material in the coke must be essentially carbon. This is an important point, since it indicates that tar formation is negligible in this case.

Now consider the various means by which it is possible to arrive at the ratio of water vapor to nitrogen in the blast. The simplest way to calculate it is from the measured dew point of the blast. Almost equally obvious is a computation based on the quantities of air and steam supplied to form the blast. Since all the hydrogen, oxygen, and nitrogen in the blast go into the producer gas, a third method can be based on element balances, working backward from the gas and correcting for contributions from the fuel. This correction requires the ratio between fuel and gas produced. Had it not been given, it could be obtained by a carbon balance, justified in this instance by the fact that tar formation is evidently very small.

Method 1. Blast dew point. At 142°F, the vapor pressure of water is 6.19 in. Hg.

$$6.19/(29.92 - 6.19)0.79 = 0.330 \text{ mol H}_2\text{O per mol N}_2$$

Method 2. Steam and air supply. At 60°F, the vapor pressure of water is 0.52 in. Hg. Choose a basis of 1 lb of dry fuel.

$$\frac{46.5(30.0)(492)(29.92 - 0.52)0.79}{359(29.9)(520)(29.92)} = 0.0955 \text{ mol N}_2 \text{ in air}$$

$$\frac{46.5(30.0)(492)(0.52)(0.80)}{359(29.9)(520)(29.92)} = 0.0017 \text{ mol H}_2\text{O in air}$$

$$0.53/18 = 0.0294 \text{ mol steam}$$

$$(0.0294 + 0.0017)/0.0955 = 0.326 \text{ mol H}_2\text{O per mol N}_2$$

Method 3. Fuel and gas analyses and amounts. The nitrogen, undecomposed steam, and decomposed steam appearing in the producer gas

can be calculated directly from the data given on the volume and composition of the gas. A convenient basis is 1 lb of dry fuel fired.

$$\frac{71.4(30.0)(492)(29.92 - 0.52)0.517}{359(29.9)(520)(29.92)} = 0.0960 \text{ mol N}_2 \text{ in gas}$$

$$0.0960(14.2/51.7) = 0.0263 \text{ mol decomposed H}_2\text{O in gas}$$

The vapor pressure of water at 100°F is 1.93 in. Hg, and the total pressure of the gas is $29.92 + (21.5 - 19.5)/13.6 = 30.07$ in. Hg.

$$\frac{0.0960(1.93)}{0.517(30.07 - 1.93)} = 0.0127 \text{ mol undecomposed H}_2\text{O in gas}$$

In order to arrive at the composition of the blast, it is now necessary to subtract contributions from the fuel. It is undoubtedly safe to neglect the nitrogen content of the coke, and therefore the value of 0.0960 mol of N₂ in the gas is substantially equal to N₂ in the blast. As shown above, net H₂ from the fuel is insignificant in this case. This makes it practically certain that combined water in the coke is also negligible, and therefore the only significant contribution of hydrogen and oxygen from the fuel is in the form of moisture.

$$9.6/(100 - 9.6)18 = 0.0059 \text{ mol H}_2\text{O as moisture in fuel}$$

The water vapor in the blast can now be found by a balance on water.

$$0.0263 + 0.0127 - 0.0059 = 0.0331 \text{ mol H}_2\text{O in blast}$$

$$0.0331/0.0960 = 0.345 \text{ mol H}_2\text{O per mol N}_2$$

It should be noted that in each of the three methods no test data other than barometer were used that were employed in either of the other two methods. The good agreement among the three answers supports the validity of the assumptions made and indicates that the operating data reported by the Rochester company were not only consistent but of an unusually high order of reliability.

Illustration 5. The following is quoted from U.S. Patent 2111579, of March 22, 1938, describing an operation of the I.G.-Winkler gas producer (see Fig. 5-3):

Referring to the drawings, (1) is a gas producer operated in the manner described in the said U.S. Patent No. 1687118 having an internal diameter of 1.1 meters and provided with brickwork (2), a grate (3), an ash stirrer (4), an ash outlet (5) and a grate chamber (6).

258 cubic meters of 95 per cent oxygen are blown in per hour through three double-walled water-cooled nozzles (7) while at the same time 935 kilograms of fine-grained brown coal small coke containing 11.2 per cent of water and 22.2 per cent of ash are forced from a bunker (9)

through a tube (10) into the gas producer by means of a worm conveyor (11). The layer of fuel is set in whirling motion up and down and has a thickness of about 1 meter. 258 cubic meters of water-gas and 40 kilograms of steam per hour are blown in below the grate (3) whereby the uniform, up and down boiling motion of the fuel is maintained. A temperature of from about 950° to 970°C is maintained in the bed of fuel by the gasification process. The watergas produced together with the circulating watergas (989 cubic meters per hour in all) leaves the gas producer through a pipe (12). Any dust carried along is partially separated

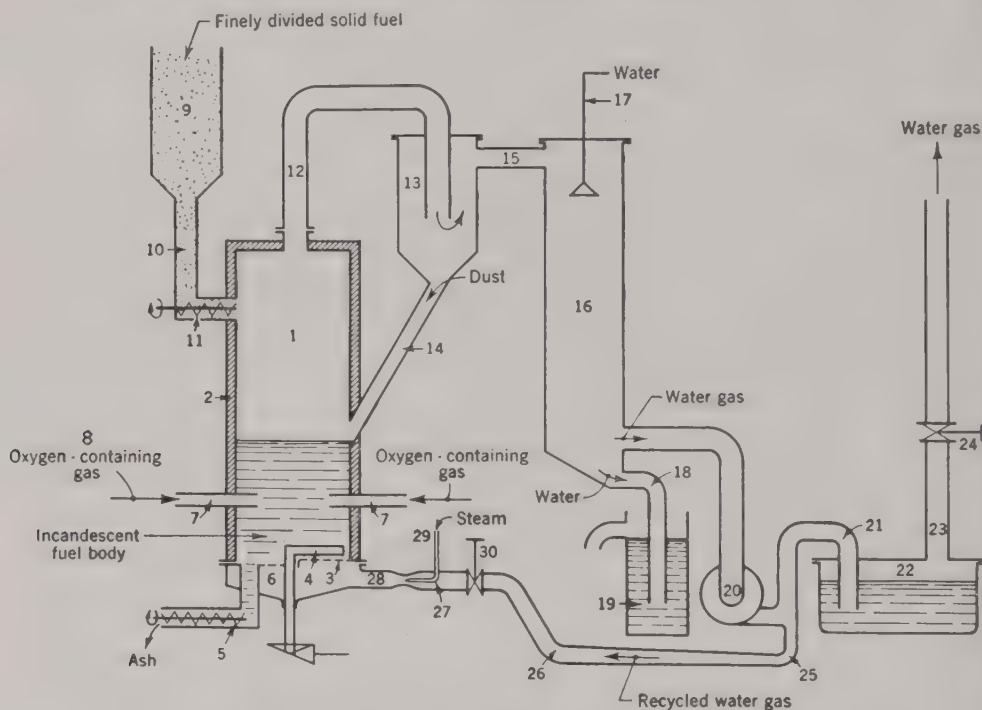


FIG. 5-3. The I. G.-Winkler gas producer.

in a dust separator (13), and slides back into the bed of fuel through a tube (14). The gas passes through a tube (15) into a washer (16) in which it is purified and cooled by means of water sprayed in at (17) and withdrawn at (18) through a receiver (19); it then passes to a blower (20) provided with water injection and from thence through a dip tube (21) into a receiver (22). 731 cubic meters of watergas per hour are withdrawn through a pipe (23) provided with a throttle slide (24) and used for any desired purpose. Before reaching the dip-tube (21), 258 cubic meters per hour of watergas are branched off at (25) by the steam injection blower (27) and forced through a pipe (28) into the grate chamber (6) below the grate (3). The steam injection blower (27) requires 40 kilograms per hour of steam heated to 400°C which is supplied at (29) under a pressure of 3.5 atmospheres. (30) is a regulating valve.

The coke in the gas producer is maintained in vigorous movement

by the watergas (258 cubic meters per hour) continuously returned in circulation. The fine ashes containing only small amounts of fine grains of slag and the sand and siliceous matter contained in the initial coke, are continually withdrawn in an amount of 90 kilograms per hour through the ash outlet (5).

The gas produced has the following composition:

13.7 per cent of CO_2
 50.6 per cent of CO
 29.5 per cent of H_2
 1.4 per cent of CH_4
 3.9 per cent of N_2 and
 2.2 grams per cubic meter of H_2S

1 cubic meter of the gas has a calorific value of 2418 kilogram calories.

From this information, what conclusions can one draw as to the operation of the unit?

Discussion. The first thing to do is to test the dependability of the data by material balances. One may well start by breaking down the gas analytical data in the conventional way, as in the first five vertical columns of Table 5-1.

TABLE 5-1. WINKLER PRODUCER GAS

Gas	Per cent	Atoms C	Mols H_2	Atoms O	Higher molal heat of combustion	Kcal per 100 kg mol $\times 10^{-5}$	Lower molal heat of combustion	Kcal per 100 kg mol $\times 10^{-5}$	$Mc^{\circ}_{p,av}$ of comp. between 960°C and 20°C	$Mc^{\circ}_{p,av}$ of mixt. between 960°C and 20°C
CO_2	13.7	13.7	27.4	11.8	1.62
CO	50.6	50.6	50.6	68,000	34.40	68,000	34.40	7.6	3.84
H_2	29.5	29.5	68,300	20.16	58,000	17.11	7.1	2.09
CH_4	1.4	1.4	2.8	212,000	2.97	191,000	2.68	14.3	0.20
N_2	3.9	7.5	0.29
H_2S	0.15	0.15	135,000	0.20	125,000	0.18	10.0	0.01
Total.....	99.25	65.7	32.45	78.0	57.73	54.37	8.05

Since the data on gas-flow rates are given in cubic meters and those on solids in kilograms, it is necessary to know the conditions of measurement of the gases. While these are not stated, the fact that the flow rates in pipes 23 and 25 add up to that in pipe 12, despite some 900°C difference in temperatures, shows that the quantities are reported at some standard condition, which may well be 0°C and normal pressure, *i.e.*, 22.4 cu m/kg mol. A clue to the conditions adopted as "standard" by the authors of the patent is furnished by the heating value reported per cubic meter, because this can be calculated from the gas analysis in terms of the kilogram-molecular volume for any set of conditions.

It is usual practice in formally reporting the results of the laboratory determination of the heating value of a gas to give the higher heating value, with water formed by the combustion condensed in the calorimeter. From the sixth and seventh vertical columns in Table 5-1, it is seen that on this basis the heating value per mol of the gas is 57,730 kcal. If this is equivalent to the reported value of 2418 kcal/cu m, the kilogram-molecular volume must be $57,730/2418 = 23.9$ cu m. This corresponds to a standard temperature of 18°C for dry gas at normal atmospheric pressure. If, however, the lower heating value of the gas is the one reported, the eight and ninth columns of the table indicate a kilogram-mol volume of $54,370/2418 = 22.46$, or within 0.3% of the value corresponding to measurement at 0°C and 1 atm absolute pressure. The whole uncertainty may well be due to minor errors in the experimental laboratory determinations of gas analysis and heating value. The usual value of 22.4 will therefore be used in further calculations.

The H_2S in the table is calculated from the fact that $2.2 \text{ g} = 2.2/34 \text{ g mols} = 1.45$ liters at standard conditions, which, in 1000 liters, is 0.15 volume per cent. Note that the analysis does not add up to 100.00%.

The data of this test differ from the information ordinarily available on the operation of a producer in that the flow rates of all the relevant gas streams are reported, presumably as the results of direct measurements. This puts one in a position to set up various material balances, which can be used as independent checks upon the inner consistency and hence the dependability of the data.

Basis: 1 hr of operation.

1. *Ash balance.* The ash in the entering coke is 22.2% of 935 kg = 208 kg. However, the ash withdrawn was only 90 kg. This means that 108 kg of ash, 57% of that in the fuel charged, is unaccounted for, a discrepancy that must not be ignored.

The combustible matter in the coke used as fuel is doubtless mainly carbon, and by assuming it such one can set up a carbon balance. However, this coke probably contains some net hydrogen, which can be estimated as usual through an oxygen balance. While this could be done in the conventional way by using a nitrogen basis, there are two strong grounds for not doing so. In the first place, the phraseology of the patent leaves the impression that the 95% value given as the purity of the oxygen may well be a rounded, approximate figure, a very small error in which would introduce a considerable degree of uncertainty in the remaining 5%. If this residue were assumed to be solely nitrogen and noble gases, it would be unsuitable as a basis for calculation because of this uncertainty. Moreover, the quantity of nitrogen in the product gas is so low that its analytical determination by the conventional methods

presumably employed is subject to an error that can be a large percentage of the amount present. Since in this operation all the gas rates were determined and reported, the oxygen balance can be set up directly.

2. *Over-all oxygen balance*, excluding oxygen as H_2O and ignoring recycle gas.

Gas in, cu m	Net O_2	Mols O_2	
258	0.95		$\frac{2}{22.4} = 21.9$ atoms O entering
		22.4	
Product gas, cu m		Kg mols	
731			$\frac{0.78}{22.4} = 25.4$ atoms O out
		22.4	

Atoms O unaccounted for = $25.4 - 21.9 = 3.5 \approx 3.5$ net mols H_2O decomposed in the unit ≈ 3.5 mols H_2 introduced into the gas by water decomposition.

3. *Hydrogen balance*.

Product gas, cu m	Kg mols	
731		$\frac{0.3245}{22.4} = 10.6$ hydrogen out, expressed as kg mols H_2 per hour
	22.4	

The net H_2 in the producer gas which comes from the fuel is therefore

$$10.6 - 3.5 = 7.1 \text{ mols} = 14.2 \text{ kg/hr}$$

4. *Carbon balance*. The carbon in the product gas hourly is

$$(731/22.4)0.657 = 21.4 \text{ kg atoms}$$

or 257 kg. The total combustible matter in the coke fired hourly is $935(1 - 0.112 - 0.222) = 623$ kg. This combustible matter doubtless contains very little combined oxygen but consists predominantly of carbon and net hydrogen. However, the amount of these two accounted for in the product gas is only $257 + 14.2 = 271$ kg, which is only

$$100(271/623) = 43.5\%$$

of the combustible in the fuel fired, leaving 56.5% of the original combustible unaccounted for.

It will be noted immediately that this fraction of combustible unaccounted for is substantially the same as the corresponding figure for ash disappeared. Granting even reasonable dependability of the data, one is forced to the conclusion that more than half the coke fed remains unburnt, presumably being blown over as dust, not recycled down pipe 14, but carried over into 16 and either washed out in the cooling water through 19 or perhaps accumulating, at least in part, in the gas-washing system of the equipment.

5. *Nitrogen balance.*

Net gas feed, cu m	Mols		
258		0.05	
	22.4		= 0.575 mol N ₂ per hour in as impurity with O ₂
Gas out, cu m	Mols		
731		0.039	
	22.4		= 1.27 mols N ₂ per hour out

The difference between these two quantities, 0.695 mol N₂ per hour, might conceivably come in as air sucked in through the interstices of the solid fuel entering through feed hopper 9. Such an effect would decrease the net hydrogen calculated above by about 11%. The discrepancy between nitrogen input and output, large though it is percentagewise, is probably due to the uncertainties of the nitrogen figures in the analyses and is without significant influence on the major over-all conclusions reached.

6. *Heat balance.* The inner consistency of the data can be further tested by an energy balance on the operation. Since no information is given on the energy effects in the gas-cooling and -washing steps, the balance must be restricted to the producer itself, together with the dust-recycling unit, *i.e.*, to those parts of the equipment shown in the drawing which lie to the left of pipes 15 and 26. In doing this, one must remember that the gas-synthesis rate in this part of the unit is the net gas-production rate, $731/22.4 = 32.6$ kg mols/hr. In contrast, the dry gas through pipe 15 is $989/22.4 = 44.1$ kg mols/hr. Meanwhile, the water entering the unit is 40 kg or 2.22 mols/hr as injector steam plus $0.112(935) = 104.7$ kg, or 5.81 mols/hr in the coke. This neglects water vapor in recycled gas or oxygen feed. Subtracting water decomposed, 3.5 mols, from the sum of these two, gives the water vapor accompanying the dry gas through pipe 15, or 4.53 mols per hr. Base (ambient) temperature is assumed to be 20°C. Unburnt combustible going through pipe 15 is $623 - 271 = 352$ kg. Assuming thorough coking of the dust blown out of the unit, owing to its high temperature, this quantity is substantially carbon. Its aver-

age specific heat over the temperature range in question (20 to 960°C) is about 0.4. The specific heat of the ash is assumed to be around 0.2.

Except for the very minor quantity of heat brought into the system by the steam as sensible and latent heat, the whole energy input is in the form of undeveloped potential heat of chemical reaction between the components of the materials fed. One could charge the system with the energy equivalent to total combustion of all the fuel fed, even though the oxygen fed is insufficient to achieve this; one would then credit the system with unburnt or partially burnt combustible leaving it. Since a large part of the combustible is completely unburnt, a convenient alternative is to ignore its potential chemical energy entirely, and this will be done. One could even debit the operation with the energy release which would result were all the oxygen fed converted to complete products of combustion, CO_2 and H_2O , but instead the unit will be charged only with the chemical heat actually released in it. This is done in Table 5-2. For heats of reaction, see Table 3-4 on page 76. Enthalpies of vaporization and of high-pressure steam are from the steam tables.

TABLE 5-2. ENERGY BALANCE ON WINKLER GAS PRODUCER
Heat contents above 20°C, water uncondensed

Heat input:

<i>Heats of chemical reactions</i>	<i>Kcal</i>
CO_2 , (32.6)(0.137)(97,000).....	433,000
CO , (32.6)(0.506)(29,000).....	478,000
CH_4 , (32.6)(0.014)(22,000).....	10,000
H_2 from H_2O , (-3.5)(58,000).....	-203,000
Chemical heat evolved.....	718,000
Sensible heat in injector steam, (2.22)(8.4)(400 - 20)...	7,000
Total heat input.....	725,000

Heat output (sensible and latent heats):

Dry producer gas, (44.1)(8.05)(960 - 20).....	334,000
H_2O , (4.53)(9.1)(960 - 20).....	39,000
Ash, (208)(0.2)(960 - 20).....	39,000
Carbon, (352)(0.4)(960 - 20).....	133,000
Latent heat supplied to water in coal, (104.7)(586).....	61,000
Losses, radiation, and unaccounted for.....	119,000
Total heat output.....	725,000

Of the heat output, by far the largest part is sensible heat in the gas and dust leaving the cyclone 13. Because specific temperatures were not available, this sensible heat has been estimated by taking the temperature at the cyclone outlet to be the same as the temperature in the bed of fuel in the producer itself. There will be some difference between these temperatures because of wall losses from the top of the producer and the cyclone and also because some of the steam- and carbon dioxide-reduction

reactions certainly occurred in these parts of the unit, causing corresponding heat absorption. Hence, the sensible-heat items are somewhat too high and the heat unaccounted for is correspondingly too low. Viewed in this light, this heat balance looks reasonable, and examination of it indicates that, other than as just pointed out, the approximations assumed in making it are unlikely to have influenced it seriously. In other words, the energy relationships confirm the general validity of the data.

7. *Equilibrium relations.* Still another test of inner consistency can be applied to these data. It is well recognized that high-temperature gases containing carbon monoxide and water vapor adjust their compositions according to the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. At combustion temperatures this reaction is so rapid that equilibrium is closely approached, especially if the gases are in contact with hot solid surfaces, which catalyze the reaction. This equilibrium relation can hence be used to test dependability of furnace data on operations involving incomplete combustion. For dependable use the gas sample must be withdrawn from the high-temperature zone and quenched rapidly to a low temperature where the reaction rate is negligible, so as to "freeze" the proportions of the gases, *i.e.*, to prevent the reaction from going to the right, owing to the effect of temperature in shifting the equilibrium proportions. Because of the relatively slow cooling that undoubtedly occurred in pipes 12 and 15 and in separator 13, one would expect the composition of the gas to correspond to the equilibrium of this so-called water-gas reaction at a temperature definitely below that in the bed of the producer 1. It is desirable to apply this test, even though it can be only approximate, because of the fact that the rate of change of the equilibrium proportions with temperature is low.

Because the number of gaseous molecules on the two sides of the reaction equation is the same, one can use either the number of the gaseous mols or the partial pressures of the individual gases when using the equilibrium constant. In this case, the former is more convenient. The analysis of the dry gas through pipe 15 is the same as that through pipe 23, and the number of mols of CO_2 , CO , and H_2 per 100 mols of that dry gas can be taken from the product-gas analysis as given. However, the mols of dry gas hourly through 15 are 44.1, and of steam, 4.53. Hence the steam per 100 mols of dry gas is $4.53/0.441 = 10.3$. Hence the value of $(\text{CO}_2)(\text{H}_2)/(\text{CO})(\text{H}_2\text{O}) = (13.7)(29.5)/(50.6)(10.3) = 0.78$. This value for the equilibrium constant corresponds to a temperature of about 890°C , again confirming the general dependability of the data.

The outstanding discrepancy about the data from the point of view of what one would consider a satisfactory operation is that apparently 57% of the fuel fired is blown out of the unit ungasified. Despite the consistency of the data as a whole, one should note that this discrepancy

depends upon a single item of the numerical quantities reported, namely, the figure for the coke fired per hour, 935 kg. For example, had this quantity been reported as 435 kg/hr, *i.e.*, changed thus in a single digit, the whole test would have been looked upon as a model of agreement and compatibility of engineering data and as a gas-producer operation giving unusually low loss as ungasified combustible.¹

Study of the calculations will make it clear that the use of the higher figure indicated by the data as possible for the kilogram-mol volume at standard conditions, 23.9 cu m, will not change results sufficiently to modify the general conclusions drawn.

This problem illustrates the point that, by proper analysis of numerical data which are available on a plant or operation, one can frequently develop conclusions and bring out important information which, for one reason or another, were not stated in the original disclosure.

Water-gas carburetion. Coal or coke can be converted easily into so-called blue water gas, a mixture containing predominantly carbon monoxide and hydrogen. The heating value of this gas is too low for economical distribution over wide areas, but it can be increased by means of carburetion.

Illustration 6. The Gas Investigation Committee of the British Institution of Gas Engineers² reports a careful test on a water-gas set in which the oil used showed by ultimate analysis 85.7% C, 12.7% H, and 0.5% S. The rest, 1.1%, may be assumed O. They found that the tar and emulsions removed from the carbureted gas contained 20.5% of all the C in the oil used, and the analyses of the dry tars averaged 91.2% C, 6.2% H, and 1.2% S, leaving 1.4% O by difference. The blue gas was 6.1% CO₂, 0.1% O₂, 38.3% CO, 50.9% H₂, 0.5% CH₄, and 4.1% N₂. The carbureted water gas was 5.2% CO₂, 5.8% illuminants, 0.1% O₂, 34.9% CO, 38.1% H₂, 10.3% CH₄, and 5.6% N₂. From these data, compute the pounds of carbon per 1000 cu ft of the final product which came from the oil and the volume of blue gas used (volume at standard conditions, which in the British gas industry correspond to a pound-molecular volume of 385.5 cu ft).

Solution. On a basis of 100 lb of oil, the C in the tar was

$$0.205(85.7) = 17.57 \text{ lb}$$

With this was $17.57(6.2/91.2) = 1.19$ lb of H, 0.23 lb of S, and 0.27 lb of O. The difference, *i.e.*, oil gasified in one way or another, is 68.13 lb of C (5.68 atoms), 11.51 lb of H₂ (5.71 mols), 0.27 lb of S (0.01 atom), and 0.83

¹ That in fact the commercial Winkler unit operated substantially as the figures in the patent show is brought out by L. L. Newman, *Ind. Eng. Chem.*, **40**, 564 (1948).

² *Gas J.*, **158**, 815 (1922).

lb of O (0.05 atom). Neglecting sulfur, the net H_2 is 5.66 mols. Hence, it appears safe to assume that carbon and net hydrogen go into the gas from the oil in the ratio of 5.68 C/5.66 H_2 .

Basis: 100 mols blue gas.

	Mols	Atoms C	Atoms O	Mols H_2
CO_2	6.1	6.1	12.2	
O_2	0.1	0.2	
CO.....	38.3	38.3	38.3	
H_2	50.9	50.9
CH_4	0.5	0.5	1.0
N_2	4.1			
Total.....	100.0	44.9	50.7	51.9
$O \approx N_2$			2.2	
$O \approx$ steam decomposed.....			48.5	48.5
Net H_2	3.4

Basis: 100 mols carbureted gas.

	Mols	Atoms C	Atoms O	Mols H_2
CO_2	5.2	5.2	10.4	
C_3H_6	5.8	17.4	17.4
O_2	0.1	0.2	
CO.....	34.9	34.9	34.9	
H_2	38.1	38.1
CH_4	10.3	10.3	20.6
N_2	5.6			
Total.....	100.0	67.8	45.5	76.1
$O \approx N_2$			3.0	
$O \approx$ steam decomposed.....			42.5	42.5
Net H_2	33.6

Call x the mols of blue gas and y the atoms of carbon in the product from the oil per mol of carbureted water gas. Set up (1) a carbon balance and (2) a *net* hydrogen balance, in each case equating the amount of the element in the blue gas plus that coming from the oil to that in the carbureted water gas.

$$\begin{aligned}
 \text{C balance:} & \quad 0.449x + y = 0.678 \\
 \text{Net } H_2 \text{ balance:} & \quad 0.034x + (5.66/5.68)y = 0.336 \\
 & \quad y = 0.309 \text{ atom C} = 3.71 \text{ lb C} \\
 & \quad x = 0.822 \text{ mol blue gas}
 \end{aligned}$$

This, however, is for 385.5 cu ft. Hence, for 1000 cu ft the carbon from the oil is $3.71(1000/385.5) = 9.61$ lb. Similarly, the blue-gas consumption is 822 cu ft per 1000 cu ft of product.

By entirely different measurements and methods the committee found 9.38 lb of C from the oil and 840 cu ft of blue gas.

This test was conducted at a carburetor temperature of about 1330°F. This is lower than the practice in many American plants. With higher temperatures, tar formation is less. Above 1400°F it is probably not far in error to assume as a first approximation that 90% of the C and 95% of the net H of the oil go into the gas. Of the remainder, however, some does not show up as tar but is burnt out during the air blow.

Illustration 7. A committee report of the American Gas Association¹ gives the following data: blue gas, 5.0% CO₂, 0.3% O₂, 38.9% CO, 51.6% H₂, 2.5% CH₄, and 1.7% N₂; finished gas, 4.1% CO₂, 10.1% illuminants, 1.0% O₂, 28.5% CO, 31.9% H₂, 14.7% CH₄, and 9.7% N₂. While they do not give the ultimate analysis of the oil, it was a mid-continent stock with a specific gravity such that it probably contained very nearly 6 lb of carbon and 0.86 lb of net hydrogen per gallon. From these data and the assumption of the preceding paragraph, compute

1. Gallons of oil used per 1000 cu ft finished gas
2. Cubic feet of blue gas per 1000 cu ft finished gas
3. Per cent of carbon present as oxides in the finished gas that entered as oxides in the blue gas

Solution. The carbon entering the product from the oil is assumed to be 90% of 6 lb = 5.4 lb = 0.45 atom C and the hydrogen, 95% of 0.86 lb = 0.817 lb = 0.405 mol H₂.

Basis: 100 mols blue gas.

	Mols	Atoms C	Atoms O	Mols H ₂
CO ₂	5.0	5.0	10.0	
O ₂	0.3	0.6	
CO.....	38.9	38.9	38.9	
H ₂	51.6	51.6
CH ₄	2.5	2.5	5.0
N ₂	1.7			
Total.....	100.0	46.4	49.5	56.6
O \approx N ₂			0.9	
O \approx steam decomposed.....			48.6	48.6
Net H ₂	8.0

¹ *Am. Gas Assoc. Proc.*, 1923, p. 1038.

Basis: 100 mols finished gas.

	Mols	Atoms C	Atoms O	Mols H ₂
CO ₂	4.1	4.1	8.2	
C ₃ H ₆	10.1	30.3	30.3
O ₂	1.0	2.0	
CO.....	28.5	28.5	28.5	
H ₂	31.9	31.9
CH ₄	14.7	14.7	29.4
N ₂	9.7			
Total.....	100.0	77.6	38.7	91.6
O \approx N ₂			5.15	
O \approx steam decomposed.....			33.55	33.55
Net H ₂	58.05

On the basis of 1 mol of finished gas:

x = mols of blue gas

y = gallons of oil

C balance: $0.464x + 0.45y = 0.776$

Net H₂ balance: $0.08x + 0.405y = 0.5805$

$x = 0.353$ $y = 1.36$

Since, in American practice, the pound-molecular volume is 380 cu ft, the oil per 1000 cu ft of product is $1.36(1000/380) = 3.58$ gal. The direct measurements of the committee showed 3.69 gal, a difference of 3%. The blue gas per 1000 cu ft of product is obviously 353 cu ft. This blue gas contained $5.0 + 38.9 = 43.9\%$ of carbon oxides, or 155 cu ft per 1000 cu ft of finished gas. Since the finished gas contained

$$4.1 + 28.5 = 32.6\% = 326 \text{ cu ft}$$

of oxides of carbon per 1000 cu ft of product, $100(155/326) = 47.5\%$ of these entered as blue gas. The rest were formed in the carburetor or superheater by reaction of the excess steam from the generator. The steam probably interacts directly with hydrocarbons, but stoichiometrically the process can be considered as water-gas formation with carbon deposited by cracking. This phenomenon is much more marked in this case than in the previous one, because of the higher temperature and the correspondingly higher reaction rate. This decomposition of steam during carburetion is a decided factor in lessening tar formation.

If, in using this method, net hydrogen in the coke could be neglected,

or if, as is frequently allowable, it is possible to assume the value of the ratio of (net H_2)/C in the generator fuel as consumed during the steam blow, it is not necessary to analyze the blue gas, but the ratio of carbon from blue gas to carbon from oil can be computed, using only the analysis of the finished gas and of the oil corrected for tar. Were there no net hydrogen in the coke, all net hydrogen in the product would come from oil alone; hence, this would be computed accurately from a net hydrogen balance. The net hydrogen in the generator fuel is only a minor correction, and hence the computed oil value is quite dependable. The quantity of blue gas is computed from a carbon balance by difference and is a much less accurate figure.

Water-gas re-forming. Catalytic conversion of water gas to hydrocarbon gas has been suggested as one possible alternative to carburetion. The sort of reactions that occur in the synthesis of secondary fuel of this type are indicated in the following problem.

Illustration 8. Haslam and Forrest¹ took a blue water gas averaging 7.6% CO_2 , 0.5% O_2 , 35.2% CO , 51.9% H_2 , 0.8% CH_4 , and 4.0% N_2 and passed it over 10 g of nickel catalyst supported on 20 g of kieselguhr brick ($\frac{1}{8}$ in. down to 10 mesh; bulk density, 0.77) at a temperature of 335°C at a rate of 120 ml/min (d.s.c.). The effluent gas was 43.8% CO_2 , 0.2% CO , 46.2% CH_4 , 6.0% H_2 , and 3.8% N_2 . Over a 28-hr period, no loss in catalyst activity was detectable. Lower gas velocity gave no further conversion, but conversion began to drop off at higher flow rates. Examination of the catalyst after the completion of the series showed no deposition of carbon. What conclusions can one draw from these data?

Discussion. The first thing to do is to break down the data in the usual way and then see what information can be procured from element balances.

Basis: 100 mols of inlet gas.

Gas	Mols	Atoms C	Mols H_2	Atoms O
CO_2	7.6	7.6	15.2
O_2	0.5	1.0
CO	35.2	35.2	35.2
H_2	51.9	51.9	
CH_4	0.8	0.8	1.6	
N_2	4.0			
Total	100.0	43.6	53.5	51.4

¹ R. T. Haslam and H. O. Forrest, *Gas Age-Record*, Nov. 17, 1923.

Basis: 100 mols of outlet gas.

Gas	Mols	Atoms C	Mols H ₂	Atoms O
CO ₂	43.8	43.8	87.6
CO.....	0.2	0.2	0.2
CH ₄	46.2	46.2	92.4	
H ₂	6.0	6.0	
N ₂	3.8			
Total.....	100.0	90.2	98.4	87.8

Since no carbon was deposited on the catalyst, the relation between the two gases can be obtained by a carbon balance. A nitrogen balance can also be employed. Neither a hydrogen balance nor an oxygen balance can be used directly because of the probability of water formation by the water-gas shift reaction, $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$. By a carbon balance, the volumetric ratio of dry inlet gas to dry outlet gas is $90.2/43.6 = 2.07$. On the basis of 100 mols of the inlet gas, *i.e.*, 43.6 atoms of carbon entering the reactor, the hydrogen in the leaving gas is $98.4(43.6/90.2) = 47.5$ mols H₂ and the corresponding oxygen is $87.8(43.6/90.2) = 42.4$ atoms. In other words, the hydrogen in the leaving gas as analyzed is less by

$$53.5 - 47.5 = 6.0 \text{ mols}$$

than the hydrogen in the entering gas, and the corresponding decrease in oxygen is $51.4 - 42.4 = 9.0$ atoms. Under the existing circumstances, practically the only possibility of reducing the amount of these two elements in the gas is by water formation, which, of course, would not show up in the dry-gas analysis. If this be the explanation, the ratio of mols of hydrogen to atoms of oxygen disappearing should be unity rather than the $6.0/9.0 = 0.67$ found above.

The discrepancy may be due simply to errors in the gas analyses. However, there probably is no oxygen as such in the inlet blue water gas as it leaves the bed of the producer. If this reported oxygen be ignored as an error, the decrease in oxygen drops from 9.0 to 8.0, raising the ratio of molecular hydrogen to atomic oxygen disappearance to 0.75.

A disturbing thing about the analyses is the fact that the nitrogen content of the exit gas is actually a little less than that of the entering gas, despite the fact that the carbon content has nearly doubled. On the basis of a carbon balance, the volume of exit gas should be about half that of the entering gas and the percentage of nitrogen in the exit gas correspondingly nearly double that in the entering gas. Another way of saying the same thing is to get the volumetric ratio of the two gas streams by a nitrogen balance. On this basis the ratio of dry inlet gas to dry outlet

gas is $3.8/4.0 = 0.95$, in contrast to the ratio 2.07 calculated above by a carbon balance.

While the nitrogens are small and analytical errors tend to accumulate in them, the discrepancy between the two values seems too large to ignore. Since the entering-gas analysis shows a relatively high content of O_2 , it is possible that both the oxygen and the nitrogen in this gas may be due to an air leak into the blue-gas sample prior to analysis. Haslam and Forrest did not give details of sampling, but if such a contamination with air is assumed, not only should the $0.5 O_2$ be eliminated (as has been already done above), but the N_2 of the blue gas itself as fed to the catalyst unit should be reduced by $0.5(79/21) = 1.9$ mols, leaving $4.0 - 1.9 = 2.1$ mols N_2 actually in the blue gas. This makes the ratio of blue gas (as actually analyzed) to product gas $3.8/2.1 = 1.81$ when calculated by a nitrogen balance, as compared with $90.2/43.6 = 2.07$ by a carbon balance. How well these ratios check is seen from the fact that, were the N_2 in the blue gas as analyzed high by an absolute amount of 0.3%, so that its actual N_2 content were 3.7% instead of 4.0%, this ratio from the nitrogen balance would exceed that from the carbon balance.¹ It is obvious that a check of this sort does not prove that the elementary oxygen reported in the blue-gas analysis was due to air contamination in sampling, but it makes one decidedly suspicious that this may have been the case.

Discrepancies of this sort in gas analytical data are common and can be minimized only by extreme care in analytical techniques. Despite the discrepancies, the magnitudes of disappearance of hydrogen and oxygen just calculated are sufficient to justify the conclusion that in the reaction here recorded significant conversion to water vapor of hydrogen and oxygen in the entering gas occurred in the operation.

Further inspection of the data makes it clear that the methane synthesized is formed stoichiometrically by the reaction of most of the original carbon monoxide with hydrogen. It is equally obvious that the oxygen thus replaced went either to CO_2 or to water vapor or both. The above calculations show that it went predominantly to form CO_2 . However, there are two possibilities as to the primary reaction, neither of which, on first view, seems more plausible than the other. These are



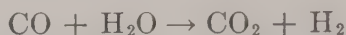
and



the water vapor of the second reaction being transformed to CO_2 by reac-

¹ In other words, in a case such as this the nitrogen balance as a method of evaluating the ratio of entering to exit gas is undependable because, in view of the analytical method employed, there is likely to be a considerable fractional error in the per cent nitrogen as determined.

tion with some of the remaining CO by the water-gas shift,



What light do the data throw on the problem of reaction mechanism?

It should be completely clear that the material balances themselves can throw no light whatever on this question. The equality of output to input is independent of reaction mechanism and reaction path. It is equally true that the over-all energy balance cannot serve for the solution of the problem. The next relationship to which one can turn is that of reaction equilibrium. The equilibrium constant of the water-gas shift is obtainable from Fig. 3-14. At the temperature in question, 335°C, it is seen from Fig. 3-14 that the equilibrium ratio, $(\text{CO}_2)(\text{H}_2)/(\text{CO})(\text{H}_2\text{O})$, is approximately 25. The ratio calculated from the analytical data of the problem is $(43.8)(6)/(0.2)(6.0)(2.07) = 106$.

The gas mixture leaving the catalyst is apparently not in equilibrium from the point of view of the water-gas shift. It contains more CO_2 and hydrogen in relation to the CO and water vapor than would correspond to equilibrium. This can be explained on the assumption that the predominant primary reaction involves formation of CO_2 rather than of water vapor and is therefore reaction (A) rather than reaction (B). Were water vapor the primary product, the actual gas composition should lie on the other side of this equilibrium, *i.e.*, the value for the equilibrium ratio calculated from the analytical data would be less than 25.

In drawing this conclusion one must keep in mind the fact that small changes in gas analyses can make large changes in equilibrium ratios computed from those analyses. No firm stand should be taken on this matter without the study of far more data than have been given in this illustration. The fact that the equilibrium ratio is very sensitive to small differences in gas composition can be made clearer by the following different approach.

Assume that the oxygen shown in the analysis of the inlet gas is due to air leak in connection with the sampling operation. Assume also that this inlet gas is passed over a catalyst at 335°C, sufficient in amount to give the same conversion of total carbon to methane shown in Illustration 8, but a catalyst of a character such that the re-formed gas leaving the catalyst bed will conform to the equilibrium of the water-gas shift reaction at bed temperature. Calculate the composition of outlet gas that would be obtained.

Take as a basis 100 mols of the inlet gas as analyzed, *i.e.*, 43.6 atoms of carbon, 53.5 mols of hydrogen, 50.4 atoms of oxygen, and 2.1 mols of nitrogen. Call the resultant mols of $\text{CO}_2 = x$, $\text{CO} = y$, $\text{CH}_4 = z$, $\text{H}_2\text{O} = u$, and $\text{H}_2 = v$. By carbon balance, $x + y + z = 43.6$. By hydrogen balance, $2z + u + v = 53.5$. By oxygen balance, $2x + y + u = 50.4$.

Since the conversion of carbon to methane is to be the same as in Illustration 8, $z/(x + y) = 46.2/44.0$. The water-gas equilibrium requires that $xv/yu = 25$. Solving,

$x = 21.17$	or	45.5% CO_2
$y = 0.094$	"	0.2% CO
$z = 22.33$	"	47.9% CH_4
$v = 0.878$	"	1.9% H_2
$\text{N}_2 = 2.1$	"	4.5% N_2
Total = 46.58	"	100.0%

Only the hydrogen differs by more than 2% from the analysis of Haslam and Forrest.

Methane Re-forming. The equilibrium relations summarized in Fig. 3-14 play an important role in processes designed to effect the partial oxidation, or "re-forming," of natural gas with steam or oxygen to produce hydrogen and oxides of carbon,¹ *i.e.*, the reversal of the reactions of the preceding illustration. Data on the reaction,



have been reviewed by Austin and Day.² The values recommended by them are given in Table 5-3. In combination with Fig. 3-14, these data are a useful guide in re-forming operations.

TABLE 5-3. METHANE-HYDROGEN-GRAPHITE EQUILIBRIUM

Temp., °C	$p_{\text{H}_2}^2/p_{\text{CH}_4}$ in atmospheres	Temp., °C	$p_{\text{H}_2}^2/p_{\text{CH}_4}$ in atmospheres
400	0.071	800	20.0
450	0.166	850	31.6
500	0.427	900	47.9
550	1.00	950	70.8
600	2.14	1000	105
650	3.98	1050	141
700	7.24	1100	190
750	12.6	1150	257

Illustration 9. Finely divided nickel supported on alumina gel is a superlative catalyst for the conversion of methane gas into its elements. It is also an excellent catalyst for the water-gas reaction (interaction of CO_2 , H_2 , CO , and H_2O). If a mixture of methane and steam is passed over this catalyst, it is "re-formed" into hydrogen and oxides of carbon. The probable reaction mechanism is the following: The methane is first

¹ So important in synthetic ammonia production (Chap. 7), etc.

² J. B. Austin and M. J. Day, *Ind. Eng. Chem.*, **33**, 23 (1941).

broken down into hydrogen and carbon. This nascent carbon is extraordinarily reactive either with hydrogen to re-form the methane or with steam or CO_2 to reduce these gases. If, however, the nascent carbon persists for even a short time, under conditions where more nascent carbon is being formed, it agglomerates into larger aggregates of carbon of far greater stability and lower reactivity than the original. Once this occurs, the activity of the catalyst is killed, so that in any practical operation this development must be avoided. This particular catalyst has no significant tendency to catalyze the formation of hydrocarbons higher than methane.

It is desired to use this catalyst for the re-formation of methane by mixing the hydrocarbon with steam and passing it over the catalyst at

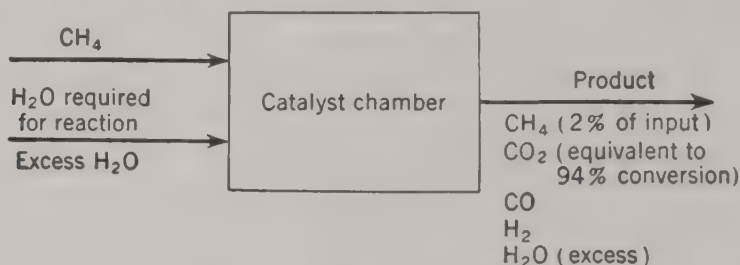


FIG. 5-4. Methane re-forming.

atmospheric pressure under conditions chosen to give, if at all practicable, a 98% total conversion of the initial methane and 94% conversion of it to CO_2 . What operating conditions are necessary to meet these requirements?

Discussion. The sketch of Fig. 5-4 will aid in visualizing the process.

Choose a basis of 100 mols of CH_4 feed. On this basis, CH_4 in the product is 2 mols, CO_2 is 94 mols, and, by carbon balance, CO is 4 mols. From a balance on oxygen, it is found that 192 mols of H_2O are consumed in the reactions. A hydrogen balance discloses that H_2 in the product is 388 mols. Thus, the only operating conditions remaining to be specified are the temperature and the mols of excess H_2O .

With a catalyst as active as is nickel in this case and a reactor designed to take full advantage of its reactivity, one can assume that the gases in the product are in substantial equilibrium with each other at the exit conditions. At any temperature the equilibrium constant K_1 for the reaction $\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$ can be obtained as the product of the constants K_2 and K_3 for the reactions $\text{CH}_4 = \text{C} + 2\text{H}_2$ and $2\text{H}_2\text{O} + \text{C} = 2\text{H}_2 + \text{CO}_2$, provided the two forms of carbon in the last two are identical. The multiplication of the *constants* is equivalent to elimination of the carbon from the last two equations by adding them. Figure 5-5 gives the values of K_1 thus calculated from the Austin and Day values for K_2 and those for K_3 from Fig. 3-14.

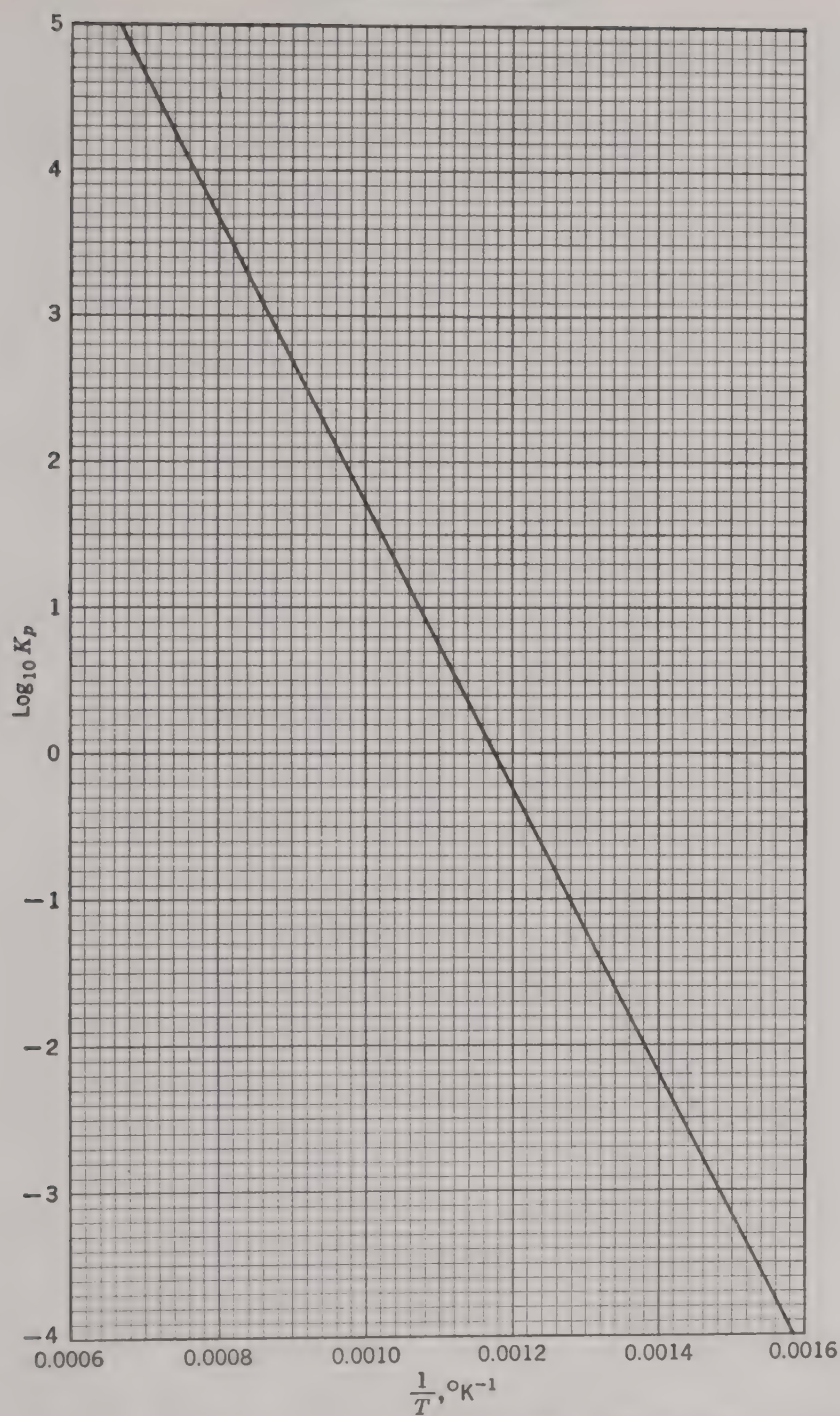


FIG. 5-5. Equilibrium constant for reaction $\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$.

Determination of the equilibrium temperature and amount of excess steam is now a matter of trial and error. A satisfactory check is obtained when it is assumed that the excess steam is 17 mols per 100 mols of CH_4 feed. The temperature determined from either K_1 or K_3 is approximately 1050°C .

The matter of carbon deposition remains to be checked. At 1050°C , according to the figures of Austin and Day, the value of $p_{\text{H}_2}^2/p_{\text{CH}_4}$ in a mixture in equilibrium with graphite is 141. In the gases produced by the re-forming operation, the actual value of

$$p_{\text{H}_2}^2/p_{\text{CH}_4} = (388)^2/(2)(2 + 94 + 4 + 388 + 17) = 149$$

This means that the composition of the exit gases does not fall within the region of carbon deposition. At first thought, it looks as though the margin of safety were extremely slim. However, one must not overlook the facts that carbon deposited by gas reactions at temperatures as low as this is never graphite, but is always in forms predominantly amorphous in character, and that these amorphous carbons are always much more active chemically than graphite. This is equivalent to saying that the value of K_2 for H_2 and CH_4 in equilibrium with carbons having activity higher than graphite will be less than the value for graphite. In other words, the margin of safety against carbon deposition is definitely greater than the difference between 149 and 141 would indicate.

PROBLEMS

1. The following analyses of experimentally made producer gases are available. In each case compute the pounds of net hydrogen in the gas per pound of carbon gasified, and state your opinion as to the probable nature of the fuel employed. Compute also for each case the pounds of water decomposed per pound of carbon gasified. In the light of the data and the results of your calculations, what is your opinion of the operation of each producer?

	Per cent				
	1 Bone & Wheeler	2 Bone & Wheeler	3 U.S. Bur. Mines	4 Am. Gas Assoc.	5 Haslam
CO_2	6.3	13.25	12.4	5.8	11.03
O_2	0.3	0.75
CO	25.7	16.05	14.0	26.0	20.35
H_2	16.8	22.65	13.8	12.1	15.63
CH_4	3.35	3.50	1.2	0.5	0.11
N_2	47.85	44.55	58.6	55.3	52.13

2. A gas producer yields a gas containing 8.0% CO_2 , 16.3% H_2 , 20.6% CO , 1.0% CH_4 , and 54.1% N_2 . The coal fired contains 70.0% C, 3.5% moisture, 7.5% ash, and negligible N and S. Tar formation can be neglected. Calculate the following quantities:

- (a) Cubic feet of gas produced (d.s.c.) per pound of coal fired. *Ans.* 70.7.
- (b) Cubic feet of air used (d.s.c.) per pound of coal fired. *Ans.* 48.4.
- (c) Pounds of steam decomposed per pound of coal fired. *Ans.* 0.278.
- (d) Ultimate analysis of the fuel. *Ans.* 6.22% H, 16.28% O.
- (e) Pounds of steam decomposed per pound of fuel fired in excess of that brought in by the fuel itself. *Ans.* 0.095.

3. The coal of the preceding problem has a heating value of 12,500 Btu/lb. The air enters the producer at 70°F with a pressure of 18 mm of water vapor. The barometer is 748 mm. The gas leaves the producer at 600°C, and its dew point is 120°F.

(a) What per cent of the heating value of the fuel appears as available heat of combustion in the gas, if the products of its combustion are cooled to room temperature? *Ans.* 77.1%.

(b) Per pound of fuel fired, how many Btu are supplied to the producer as steam? Assume that the temperature of the boiler feedwater is 70°F and that the steam is dry and saturated at barometric pressure. *Ans.* 560.

(c) If one assumes that all the water in the fuel is driven off as such and that the moisture in the entering air is decomposed in the same proportion as the steam, what per cent of the steam supplied is decomposed in the producer? *Ans.* 49.1%.

4. A coke-fired gas producer yields a gas containing 8.1% CO_2 , 23.3% CO , 5.9% H_2 , 0.2% CH_4 , and 62.5% N_2 , as shown by Orsat analysis. The coke contains 78.1% C and 3.0% moisture, and the steam used amounts to 0.52 lb per pound of coke. Calculate the following quantities:

(a) Cubic feet of wet gas at 500°C and normal atmospheric pressure per pound of coke fired.

(b) Cubic feet of dry air at 85°F and normal atmospheric pressure per pound of coke fired.

(c) Per cent of steam input decomposed in the producer. Assume that the moisture in the coke is driven off without decomposition.

(d) The higher heating value of the total gas produced, expressed as a percentage of the higher heating value of the total fuel fired.

5. Haslam and co-workers¹ studied the effect of certain major operating variables on the performance of a gas producer. In all tests they used anthracite of the following analysis: 2.35% moisture, 7.70% volatile matter, 76.55% fixed carbon, 13.40% ash, 78.84% C, heating value 12,690 Btu/lb. Each test was a batch operation in that, just before the test in question, the producer was charged to the desired depth of fuel with fresh anthracite and then blown with air sufficiently to bring even the top of the fuel bed to dull red heat. The rates of air and steam were then carefully adjusted and the unit allowed to operate for the short period of time necessary to bring it to steady state conditions. The gas samples were then taken and the other observations made. In the following table are found the data for six of the runs.

¹ R. F. Mackie and F. H. Reed, M. S. thesis in chemical engineering, Massachusetts Institute of Technology, 1925; Cf. R. T. Haslam, R. F. Mackie, and F. H. Reed, *Ind. Eng. Chem.* **19**, 119 (1927); R. T. Haslam, J. T. Ward, and R. F. Mackie, *Ind. Eng. Chem.* **19**, 141 (1927).

	Run number					
	1	2	3	9	10	103
Gas analysis, per cent by volume:						
CO ₂	8.4	11.66	4.73	5.96	6.19	11.40
O ₂	0.8	0.23	0.21	0.10	0.10	0.00
CO.....	21.2	16.15	28.90	26.65	26.00	19.40
H ₂	7.9	6.67	8.40	10.56	9.76	16.00
N ₂	61.7	65.12	57.76	56.73	57.79	53.10
CH ₄	0.0	0.17	0.00	0.16	0.10
Dry air, mols/hr.....	10.5	27.1	18.8	18.4	18.5	8.70
Absolute blast pressure, mm Hg.....	760.7	767.5	755.8	768.4	765.9	760.3
Blast temperature, °F.....	123.8	122.3	123.1	125	123.8	146.0
Maximum fuel bed temperature, °F....	1,900	1,910	2,390	2,460	2,400	2,150
Exit gas temperature, °F.....	1,650	1,320	1,620	1,900	1,640	1,350
Fuel bed thickness, ft.....	1.40	1.75	1.67	2.66	3.83	2.60

Calculate the following items for each run:

- Mols of dry air fed per pound of carbon gasified.
- Mols of water vapor in the gas per 100 mols of dry gas. Assume that the blast is saturated with water vapor.
- Mols of water vapor in the gas per 100 mols of dry gas, calculated on the assumption that the exit gas is at equilibrium with respect to the water-gas reaction.
- Per cent decomposition of the steam. In this and succeeding calculations assume that the blast is saturated with water vapor.
- Lower heating value of the gas, expressed as Btu per cubic foot of gas at 60°F and 30 in. Hg abs, saturated with water vapor.
- Cold efficiency, defined as the higher heating value of the gas produced during the course of a run, expressed as a percentage of the higher heating value of the fuel consumed during the same period.
- Heat loss by radiation, convection, and conduction to the surroundings, expressed as a percentage of the total heat supplied to the unit. Employ a base temperature of 60°F with water in the liquid state.

6. A high-volatile coal containing 72.03% C, 8.98% H, 7.99% O, 1.38% N, 1.62% S, and 8.00% ash is fed to a gas producer. The entering air is at 27°C and practically dry, and the barometer is 753 mm Hg. Steam is supplied at the rate of 0.49 lb steam per pound of coal. The producer gas is carefully analyzed by the conventional Orsat technique and found to contain 5.68% CO₂, 23.37% CO, 1.61% CH₄, 28.94% H₂, and 40.40% N₂. The partial pressure of water vapor in the gas is 30.2 mm Hg. Examination of the refuse indicates that it is substantially free of combustible matter. Calculate the following:

- The mols of air supplied per pound of coal fired.
- The per cent of the carbon fired appearing in the tar.
- The composition of the tar.

7. A gas producer is fired with a coal having the following ultimate analysis: 68.0% C, 6.5% H, 1.5% N, 1.2% S, 13.8% O, and 9.0% ash. The refuse is substantially free of both moisture and sulfur, but contains some unburnt carbon. The gas analysis, determined carefully in an Orsat apparatus with mercury as the confining liquid, is reported as 13.0% CO₂, 16.2% CO, 3.2% CH₄, 23.0% H₂, and 44.6% N₂. Air enters the producer at 75°F with a partial pressure of water of 12 mm. The barometer is

750 mm. The unit uses 0.95 lb steam per pound of coal fired. The gas leaves the producer at 560°C and substantially barometric pressure, with a partial pressure of water of 145 mm.

(a) What is the volume of dry gas produced (measured at 32°F and 1 atm) per 100 lb of coal fired?

(b) Calculate the pounds of steam decomposed per 100 lb of coal fired.

8. A gas producer is charged with a coal containing 75.6% C, 4.9% ash, and 3.0% moisture, with negligible nitrogen and sulfur. The resulting gas has the following average Orsat analysis: 9.8% CO₂, 0.2% C₂H₄, 18.4% CO, 12.9% H₂, 3.1% CH₄, and 55.6% N₂. The formation of tar, containing 12% water, is 190 lb per ton of coal used. The dry tar is composed of 88% C and 12% H. The refuse is thoroughly burnt. The air enters with a partial pressure of water vapor of 18 mm, while the barometric pressure is 750 mm. The gases leave the producer at 1300°F with a partial pressure of water vapor of 140 mm. Calculate the following quantities:

(a) Cubic feet of producer gas (d.s.c.) per pound of coal fired.

(b) Cubic feet of air (d.s.c.) per pound of coal fired.

(d) Pounds of steam, as such, supplied to the producer per pound of coal fired.

(e) Per cent decomposition of the steam.

9. A pressure-type gas producer is being fired with a bituminous coal having a heating value of 14,010 Btu/lb and containing 78.8% C, 6.6% ash, and 2.8% moisture. Coal from the same field is known to average 1.3% N and 0.2% S. The analysis of the dry producer gas is 11.2% CO₂, 16.9% CO, 1.1% O₂, 17.1% H₂, 1.7% CH₄, and 52.0% N₂. Production of tar, averaging 10% water, is 80 lb per ton of coal fired. The dry tar contains 89% C and 11% H. Soot (practically pure carbon) amounts to 50 lb per ton of coal fired. The dry refuse contains 9% combustible, all carbon. The temperature of the air is 75°F, and the partial pressure of water vapor in the air is 8.8 mm Hg. The gases leave the producer at 1100°F. At atmospheric pressure a sample of the gases has a partial pressure of water vapor of 158 mm Hg. The barometer is 755 mm Hg. Calculate the following:

(a) Ultimate analysis of the fuel.

(b) Pounds of steam, as such, supplied to the producer per pound of coal fired.

(c) Per cent of steam supplied that is decomposed in the producer.

(d) Cubic feet of gas (d.s.c.) leaving the producer per pound of coal fired.

(e) Cold efficiency, defined as the higher heating value of the total gas, expressed as a percentage of the higher heating value of the total fuel.

10. The American Gas Association reports the following data obtained as the result of a test on a coke-fired producer in a Chicago plant (all gas quantities are at dry, standard conditions):

Primary air, cu ft per pound of fuel.....	51.8
Barometer.....	Normal
Dew point of air blast, °F.....	137
Producer gas, cu ft per pound of fuel.....	73.3
Steam, lb per pound of fuel.....	0.646
Steam, lb per pound of air.....	0.163

Fuel and cinder analyses:

	Coke	Cinder
Moisture (as fired).....	10.90	
Volatile combustible matter (dry basis).....	1.88	
Fixed carbon (dry basis).....	88.27	9.97
Ash (dry basis).....	9.85	90.03
Heating value, Btu/lb (as fired).....	12,605	

Producer gas: 5.8% CO_2 , 0.3% O_2 , 26.0% CO , 12.1% H_2 , 0.5% CH_4 , 55.3% N_2 . A considerable portion of the fuel was in the form of fines. For each pound of coke fired, 0.12 lb of fines was blown out as dust in the producer gas and collected in a dust catcher on the gas line. The dust contained 1.7% moisture, 87.04% combustible matter, and 11.26% ash. From these data calculate the steam supply in the air blast, expressed as mols of steam per 100 mols of dry producer gas, by five independent methods of computation, *i.e.*, using in each case some item of basic data or information not employed in any of the other methods of computation.

11. The following questions refer to the gas producer of Illustration 5:

(a) What would be the standard temperature of measurement of the heating value of the gas, if the determination were made on gas saturated with water vapor, rather than on dry gas, and the reported figure were the higher heating value? The lower heating value?

(b) On the assumption that the excess N_2 shown in the balance all came from air entrapped in the powdered coal fed as fuel, estimate the amount of air thus introduced, in cubic meters per hour, and the air velocity in feet per second through the feed pipe past the fuel. Assume that the reactor was operated under a slight suction to prevent the loss of producer gas.

(c) What is the linear velocity in feet per second of the gases leaving the top of the reactor? Consider the linear velocity to be the volumetric flow rate divided by the cross-sectional area of the producer.

12. A powdered coal, the average ultimate analysis of which is 78% C, 5% H, 1% N, negligible S, and 10% ash, is fed continuously into a deep bed of the powder up through which air is blown for its combustion. The mixing of the powder in the bed is substantially perfect. The temperature of the bed is quite constant at 800°C . The coal is fed at a constant rate, and the solid residue is withdrawn continuously from the bed at a rate sufficient to maintain the amount of solid in the bed constant. The residue withdrawn contains 50% ash. The air is introduced at a rate such that its linear velocity upward into the bed after it has reached bed temperature but before any significant reaction has occurred is 0.8 ft/sec. Estimate the composition of the gas leaving the top of the bed and its linear velocity.

13. A plant engaged in low-temperature carbonization has a battery of by-product coke ovens, which is fed with coal containing 3.13% moisture, 32.96% volatile matter, 56.41% fixed carbon, and 7.50% ash as charged, with an ultimate analysis on the same basis of 74.99% C, 5.35% H, 0.90% S, 1.49% N, 9.77% O, and 7.50% ash. The operation produces a gas the average composition of which after removal of H_2S is 2.8% CO_2 , 0.6% O_2 , 8.4% CO , 3.3% illuminants, 47.3% H_2 , 25.2% CH_4 , 1.0% C_2H_6 , and 11.4% N_2 . The illuminants may be assumed to be propylene. The tar produced amounts to 12 gal per ton of coal charged, has a specific gravity of 1.2, and contains approximately 92% C and 8% H. Estimate the following:

(a) The yield of gas per ton of coal charged, expressed as cubic feet of gas at 60°F and 30 in. Hg, saturated with water vapor.

(b) The pounds of coke produced per ton of coal charged.

14. The following data are average operating results over a period of 1 month for three 11-ft blue-gas sets.¹ Gas volumes are measured at 30 in. Hg and 60°F , saturated with water vapor. Material per 1000 cu ft of blue gas: dry coke, 34.7 lb; carbon content of coke, 32.0 lb; carbon lost to clinker heap, 4.05 lb; steam (12 psig), 51.9 lb; air, 2235 cu ft. Analysis of coke: 4.2% moisture, 2.69% volatile matter, 89.80% fixed carbon, 7.51% ash, heating value 13,200 Btu per pound of dry coke. Analysis of blue gas: 5.4% CO_2 , 0.7% O_2 , 37.0% CO , 47.3% H_2 , 1.3% CH_4 , 8.3% N_2 .

¹ W. R. Morris, *Am. Gas Assoc. Proc. Tech. Sessions*, 1922, 21-52.

Analysis of blast gas entering the waste-heat boiler: 19.9% CO_2 , 1.1% O_2 , 79.0% N_2 . Average temperature of blue and blast gases: entering the waste-heat boiler 1,300°F; leaving the waste-heat boiler, 550°F. The steam pressure in the waste-heat boiler was 150 psig. Calculate from these data the following quantities:

(a) Per cent of carbon in the fuel that is gasified by the steam and the per cent gasified by the air.

(b) Per cent of steam fed that is decomposed.

(c) Mols of dry blast gas per 1000 cu ft of blue gas. Compute this quantity by two independent methods, *i.e.*, using in each case some principle or item of data or information not employed in the other method of computation.

(d) Cold efficiency, defined as the higher heating value of the blue gas expressed as a percentage of the higher heating value of the fuel plus the heat in the steam supplied to the grate, relative to liquid water at 60°F.

(e) Pounds of steam generated in the waste-heat boiler per 1000 cu ft of blue gas. Assume that 3% of the heat given up by the blue and blast gases as they pass through the boiler is lost to the surroundings by radiation, etc. Assume that the temperature of the boiler feed is 60°F and the boiler delivers saturated steam.

(f) Hot efficiency, defined as the higher heating value of the blue gas plus the heat absorbed in generation of steam in the waste-heat boiler, expressed as a percentage of the higher heating value of the fuel plus the heat in the steam supply relative to liquid water at 60°F.

15. In a laboratory investigation steam was reacted with dry coke in a fluidized powder bed at 1900°F. The coke contained 13.7% ash and negligible volatile matter. The fusion temperature of the ash was 2450°F. The average height of the powder bed was 30 in., and the velocity of the steam as it entered the bottom of the bed was 0.65 ft/sec, based on the free cross-sectional area of the reactor. After removal of H_2S , the blue gas leaving the top of the powder bed was found to contain 1.7% CO_2 , 0.2% O_2 , 48.0% CO , 0.3% CH_4 , 48.7% H_2 , and 1.1% N_2 . The partial pressure of water vapor in the blue gas was 29.2 mm Hg, and the total pressure was 32.4 in. Hg.

The proposal has been made to carry out the same reaction as in the above operation in two reactors instead of one. In the first reactor fresh coke would be fluidized by and reacted with steam. In the second reactor spent coke (*i.e.*, coke with a carbon content intermediate between that of fresh coke and coke from which all carbon has been gasified) from the first reactor would be burnt with air. The heat generated in the second reactor would be transferred to the first reactor to furnish the heat required.

Assume that the theoretical quantity of air will burn substantially all the carbon from the spent coke in the second reactor and that all the gas streams leaving the reactors can be cooled to 550°F by passing them through a waste-heat boiler, which will generate saturated steam at 150 psig from water at 60°F. Assume that the steam supplied to the first reactor is drawn from a main under a pressure of 12 psig.

Estimate for the proposed setup the items of information requested in parts (a), (b), (d), (e), and (f) of Prob. 14; and compare the proposed setup with that of Prob. 14. What are your recommendations?

16. As a step in the manufacture of hydrogen for use in a synthetic-ammonia plant, water gas is being converted with superheated steam over an iron oxide catalyst at 300°C. The water gas fed to the converter contains 4.5% CO_2 , 1.2% O_2 , 40.4% CO , 49.4% H_2 , and 4.5% N_2 , while the average analysis of the gas leaving the converter is 27.8% CO_2 , 0.9% O_2 , 6.1% CO , 61.8% H_2 , and 3.4% N_2 . Calculate the following items of information:

(a) Mols of dry water gas per pound of carbon in the coke charged to the water-gas set.

(b) Pounds of steam decomposed in the water-gas set per pound of carbon in the coke.

(c) Mols of dry converter gas per mol of dry water gas.

(d) Pounds of steam decomposed in the converter per mol of dry water gas.

17. If the same blue gas and operating conditions as in Illustration 8 are employed, how many pounds of nickel and what size of converter (in cubic feet) would be required for production of CO_2 -free product gas (*i.e.*, after removal of CO_2) at the rate of 1,000,000 cu ft per 24 hr, measured at 60°F , 30 in. Hg, saturated with water vapor? If the blue gas enters the converter at converter temperature, how much heat must be removed hourly by the cooling coils?

18. Assume that the reported analysis of the inlet gas of Illustration 8 is correct, but that it contains water vapor as it enters the catalyst bed. Assume that the catalyst not only promotes the methane synthesis but is also sufficiently active in catalyzing the water-gas shift so that it brings the exit gases substantially to the equilibrium of this shift at the bed temperature of 335°C . Assume, furthermore, that the water content of the inlet gases is such that, under the above conditions, the exit gases will in fact show on analysis 0.2% CO and 6.0% H_2 . Calculate the following:

(a) The complete analysis of the exit gases (dry basis).

(b) The dew point of the exit gases. Assume that the bed operates at atmospheric pressure.

19. An equimolal mixture of CO and steam at a total pressure of 1 atm is to be passed over a catalyst for conversion to H_2 .

(a) Calculate the temperature range over which there is danger of carbon deposition. Neglect the possibility of methane formation.

(b) Considering also the possibility of methane formation, investigate the danger of depositing carbon, if the gas leaves the catalyst bed at a temperature of 550°C .

20. The conventional commercial method for building up the heating value of blue water gas for use as city gas is carburetion of the gas by passing it over hot checker-brick on which gas oil (a middle- to high-boiling petroleum cut) is sprayed to crack the oil to gaseous hydrocarbons. The Btu per cubic foot can thus be raised from about 300 up as far as 500 to 650, depending on conditions. Because in recent years the cost of suitable gas oil has risen greatly, the suggestion has been made that water gas be raised in heating value by passing it over metallic nickel to catalyze its conversion to methane. As a preliminary test of the idea, a vertical stainless-steel catalyst tube, 1.25 in. I.D. and 4 ft 8 in. high, was set up. The tube was charged with 96 g of catalyst consisting of completely reduced metallic nickel deposited on silica gel powder. The nickel content of the catalyst was 30 wt-%. The tube was so heated by electric winding surrounded by insulation that its temperature could be held substantially constant throughout its length. A dry mixture of CO and H_2 flowed up through the tube. The inlet gas was preheated to catalyst temperature before entering the catalyst bed. The flow rate of the gas was kept adjusted so that it entered the bed at the bottom at a linear velocity of 1.2 ft/sec. The pressure was substantially atmospheric. The temperature of the bed was adjusted at the start to 472°C and gas allowed to flow through it until the outlet gas composition had settled down to a substantially constant value. This condition was reached quickly. Inlet- and outlet-gas samples were taken and analyzed. The tube temperature was then dropped progressively to a new constant level at which, after steady conditions had developed, a second set of gas samples was taken. After a similar period, a third set of samples was taken. The supply of feed gas gave out in the interval between the first and second set of samples, and a new feed had to be substituted. Throughout the runs catalyst powder was supported by the upflowing gas as a dense, highly turbulent cloud about 26 in. deep. The gases were carefully analyzed, and the analyses are believed to be dependable. Analyses of duplicate samples checked. The CO_2 , O_2 , and CO were determined by absorption, H_2 by selective oxidation with copper oxide, and

hydrocarbon by slow combustion with O_2 . The reported values of CH_4 check the slow combustion data as to volume shrinkage, CO_2 formed, and O_2 consumed well within the precision of the measurements. The results of the experiments are summarized in the table below:

Set of samples.....	1	2	3
Bed temperature, $^{\circ}C$	472	349	330
Inlet-gas analysis:			
CO_2	0.94	0.20	0.20
O_2	0.56	0.56
CO	49.52	37.30	37.30
H_2	47.65	58.40	58.40
N_2	1.89	3.54	3.54
Btu/cu ft.....	310	306	306
Outlet-gas analysis:			
CO_2	37.38	31.85	22.50
O_2	1.96	0.37	0.18
CO	4.67	3.01	15.27
H_2	17.76	12.88	16.60
CH_4	27.10	45.80	44.44
N_2	11.13	6.09	1.01
Btu/cu ft.....	341	507	544

Analyze these data. Present a tentative opinion, based on your results, of the potentialities of the proposed process and what appear to be the best conditions under which to carry it out.

Chapter 6

SULFUR COMPOUNDS

The sulfur used in industry is derived either from the element itself or from some sulfide ore, such as pyrites. Before conversion into other compounds, these are usually burnt to give SO_2 . The operations are similar in principle to the combustion of carbon compounds, although special furnaces have to be employed. Data on the heats of formation and heat capacities of sulfur, pyrites, and some of the important compounds derivable therefrom are summarized in Table 6-1. Average heat capacities computed from the equations in the table are presented in Fig. 6-1.

Combustion of sulfur. While the main product of the primary combustion of sulfur is the dioxide, it is apparently impossible to avoid formation of some trioxide. Normally, from 2 to 10% of the sulfur burnt is oxidized to the hexavalent state.¹ The vapor pressure of SO_3 is too high to allow it to condense as such at atmospheric pressure and temperature when formed by air oxidation even if conversion to SO_3 were complete, but when it combines with water to form H_2SO_4 its condensation is quantitative. Since the usual gas analysis is carried out with saturated gas, SO_3 is removed from the gas as H_2SO_4 before analysis starts. Hence, as water vapor is eliminated from the result in the analysis of combustion gases, so any SO_3 formed does not appear in the analysis of sulfurous gases. As in the former case, however, water formed by oxidation of hydrogen can be determined by oxygen disappearance, so too, in this case, SO_3 can be computed in the same way. In both cases, this is possible because the oxygen supply is determined by the nitrogen in the gas, since all the oxygen comes in as air with a fixed O_2/N_2 ratio, and because all other products of oxidation appear in the gas analysis. Hence the oxidation product that disappears can be determined by difference.

Assume that 10 atoms of S are burnt with 100 mols of air and that 90% of the S goes to SO_2 and the rest to SO_3 . The reactions involved are

¹ In the manufacture of bisulfites it is important to keep this percentage low, while in a sulfuric acid plant it may well be high.

TABLE 6-1. THERMAL PROPERTIES OF SULFUR AND RELATED COMPOUNDS

Compound	Molal heat of formation from the elements in their standard states, measured at 18°C and constant pressure, cal/g mol ¹	Molal heat capacity at constant pressure, cal/(g mol)(°C) $T = ^\circ\text{K}$	Temperature range, °K	Ref.
S ₂ (gas).....	-29,200			
S ₆ (gas).....	-22,600			
S ₈ (gas).....	-20,000			
SO ₂ (gas)....	70,920	$6.147 + 13.844 \times 10^{-3}T - 91.03 \times 10^{-7}T^2 + 2.057 \times 10^{-9}T^3$	298.1-1800	2
SO ₃ (gas)....	93,900	$3.603 + 36.310 \times 10^{-3}T - 288.28 \times 10^{-7}T^2 + 8.649 \times 10^{-9}T^3$	298.16-1200	3
SO ₃ (liq.)....	104,200			
H ₂ SO ₄ (liq.)..	193,750	$1.42 + 0.0016t$, where $C_p = \text{joules/(g)}(^{\circ}\text{C})$, $t = ^{\circ}\text{C}$	283-318	4
H ₂ S ₂ O ₇ (liq.)..	299,600			
FeS ₂	35,500	$10.7 + 13.36 \times 10^{-3}T$		
FeS.....	23,100	$\left\{ \begin{array}{l} 2.03 + 39.0 \times 10^{-3}T \text{ (below } 411^{\circ}\text{K)} \\ \text{Heat of transition at } 411^{\circ}\text{K} = 1050 \text{ cal/g mol} \\ 12.05 + 2.73 \times 10^{-3}T \end{array} \right.$	273-773 273-411	5
Fe ₂ O ₃	198,500	$24.72 + 16.04 \times 10^{-3}T - 4.234 \times 10^5/T^2$	411-1468	5
Fe ₃ O ₄	266,900	$41.17 + 18.82 \times 10^{-3}T - 9.795 \times 10^5/T^2$	273-1097	5
FeO.....	64,300	$12.62 \times 1.492 \times 10^{-3}T - 0.762 \times 10^5/T^2$	273-1065	5
			273-1173	5

1. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

2. H. M. Spencer and G. M. Flannagan, *J. Am. Chem. Soc.*, **64**, 2511 (1942).

3. H. M. Spencer, *J. Am. Chem. Soc.*, **67**, 1859 (1945).

4. International Critical Tables, Vol. V, p. 114, McGraw-Hill Book Company, Inc., New York, 1929.

5. K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934).

$S + O_2 = SO_2$ and $2S + 3O_2 = 2SO_3$. Thus, 9 mols O_2 are consumed to form 9 mols of SO_2 , and 1.5 mols O_2 to yield 1 mol SO_3 . The remaining O_2 is $21.0 - 10.5 = 10.5$ mols. Since the SO_3 is condensed prior to analysis, the residual gas consists of 9 mols SO_2 , 10.5 mols O_2 , and 79 mols N_2 , or a

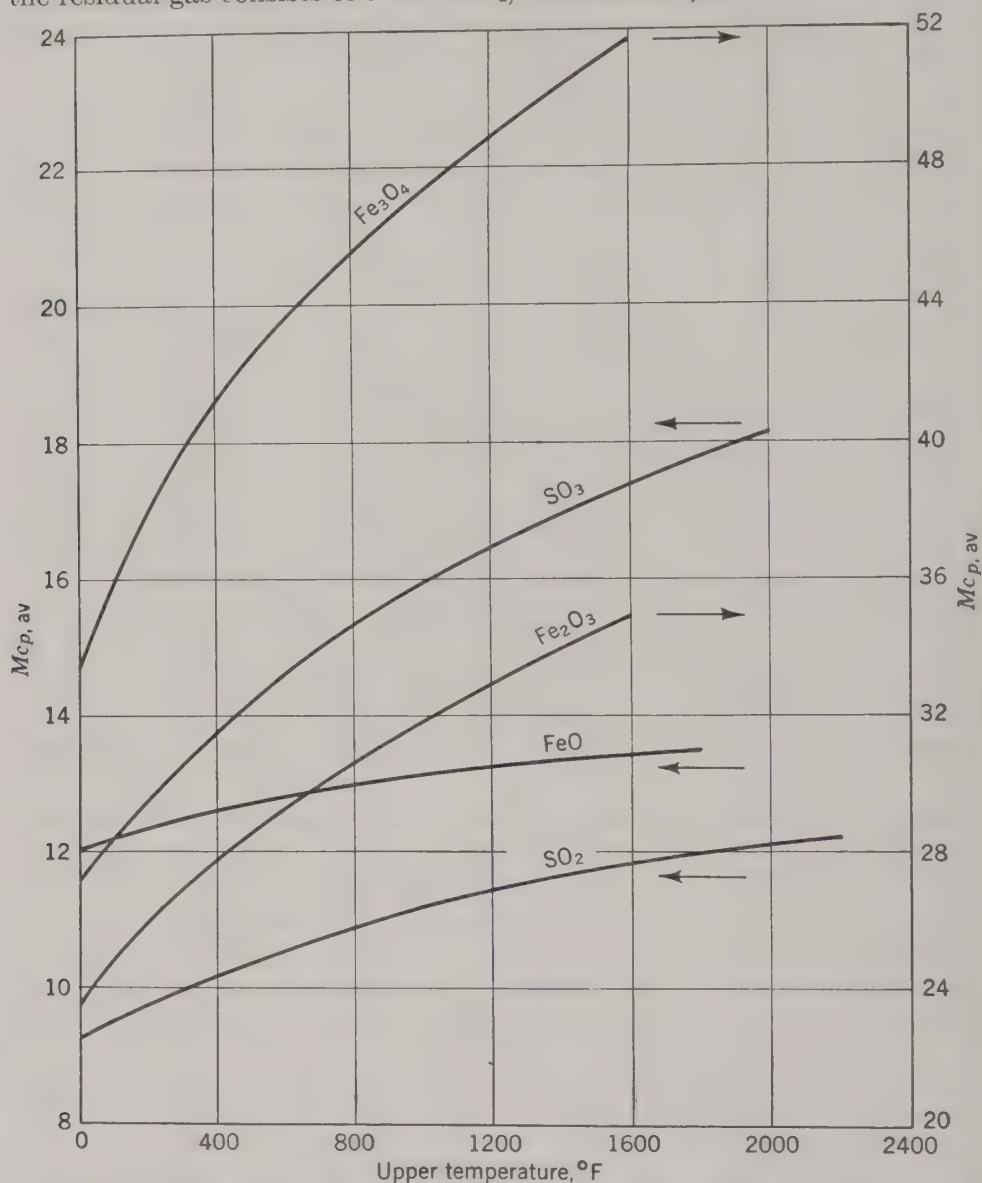


FIG. 6-1. Average molal heat capacities of iron and sulfur oxides between 60°F and abscissa temperature.

total of 98.5 mols. Hence the gas analysis shows 9.14% SO_2 , 10.66% O_2 , and 80.2% N_2 .

Calculations based on gas analysis. In practice, the gas analysis is determined experimentally and from this the per cent of sulfur burnt to

SO₃ may be computed. The preceding computation must, therefore, be reversed. Assuming the same analysis, the method is as follows:

Basis: 100 mols gas as analyzed.

Gas	Mols	Mols O ₂
SO ₂	9.14	9.14
O ₂	10.66	10.66
N ₂	80.2	
Total.....	100.00	19.80 O ₂ accounted for
80.2(21/79).....		21.32 O ₂ from air
		1.52 O ₂ to SO ₃ or 1.01 mols SO ₃

Total S burnt, $9.14 + 1.01 = 10.15$

Per cent of S as trioxide, $(1.01/10.15)100 = 9.95\%$

The failure to check perfectly is due to the fact that the estimation of the SO₃ depends upon a small difference between relatively large quantities, and the cumulative error due to rounding off the second decimal place throws out the result. Careful gas analyses are essential if the results are to be dependable, but the percentage error involved in calculating the sulfur distribution is serious only when the fraction of sulfur going to SO₃ is small.

In the important case of the use of gas analyses to determine SO₃ formation in individual units of a sulfuric acid plant, a valuable check is secured upon the results by using sulfur disappearance and oxygen decrease independently in the computations. They should be in the ratio $\frac{1}{2}\text{O}_2/1\text{S}$, and divergence from this ratio is an indication of error. Thus, the average composition of the gas entering a contact unit over a 12-hr test period is found by analysis to be 7.2% SO₂, 13.2% O₂, and 79.6% N₂, and that leaving the unit is found to be 2.8% SO₂, 11.7% O₂, and 85.5% N₂. Of the SO₂ entering this unit, what per cent is oxidized to SO₃ in it?

Since the nitrogen goes through this operation unchanged, it should be used as the basis of computation. The following tabulation is self-explanatory:

Basis: 100 mols N₂.

Gas	Mols in entering gas	Mols in exit gas	Decrease	Equivalent SO ₃
SO ₂	9.05	3.28	5.77	5.77
O ₂	16.58	13.69	2.89	5.78

Hence, of the entering 9.05 mols of SO_2 , $(5.77/9.05)100 = 63.8\%$ is oxidized to SO_3 . Furthermore, the ratio of SO_2 decrease to oxygen decrease checks within 0.2%, giving independent confirmation of the dependability of the analyses.

Elimination of nitrogen oxides. When the preceding method of calculation is to be applied to chamber gases, nitrogen oxides must be eliminated. This is easily done by collecting the gas samples through bubblers containing H_2SO_4 to absorb these oxides. Prior to taking the sample itself, enough gas should be drawn through the absorption train to saturate the absorbing acid with SO_2 at its partial pressure in the gas, in order to avoid loss of SO_2 before analysis. This is easily done and, at the same time, an average sample assured by drawing continuously an excess of gas through the absorbers by means of an aspirator and withdrawing only a fraction of this washed gas for analysis. The decrease in the ratio of SO_2/N_2 may then be taken as a quantitative measure of the acid formation between the sampling points. The oxygen decrease will not check this unless the O_2/N_2 ratio in the eliminated nitrogen oxides that are dissolved in the absorbing acid is the same at each sampling point, but since the amount of these oxides is not excessive and the ratio does not vary greatly, the error is usually negligible. This statement does not apply if the computation is carried back to the original air, since the nitrogen oxides that are absorbed in H_2SO_4 do not normally have the same O_2/N_2 ratio as do the materials added to make up nitrogen losses. Errors due to N_2O formation and to any possible reduction of active nitrogen to the element are also usually negligible.

Illustration 1. A plant burns sulfur which is 99.4% pure at the rate of 680 lb per hour. The average air temperature is 60°F . The gases emerge from the burner at 760°C and are found to contain 17.4% SO_2 and 2.7% O_2 when analyzed¹ in the usual way. The gases then pass to a cooler, which reduces their temperature to 70°F by means of water which rises from 58°F to 90°F .

Calculate:

1. The per cent of the sulfur burnt to SO_3
2. The pounds per hour of SO_2 leaving the burner
3. The air consumption in cubic feet per minute
4. The cubic feet per minute of gas leaving the burner and the cubic feet per minute leaving the cooler
5. The heat dissipated from the burner in Btu per hour
6. The water used in the cooler in gallons per hour

¹ Mercury must be used on account of the marked solubility of SO_2 in water, but a single drop of water is kept above the mercury to saturate the gas.

Solution.

Basis: 100 mols of gas as analyzed.

Gas	Mols	Mols O ₂
SO ₂	17.4	17.4
O ₂	2.7	2.7
N ₂	79.9	
Total.....	100.0	20.1 O ₂ accounted for
79.9(21/79).....		21.21 O ₂ from air
		1.11 O ₂ disappearance

$$S \text{ to } SO_3 = (2/3)1.11 = 0.74 \text{ atom S} = 0.74 \text{ mol } SO_3$$

1. *Per cent of sulfur burnt to SO₃.* Since for every 17.4 mols of SO₂ produced, 0.74 mol of SO₃ is formed, $100(0.74)/(17.4 + 0.74) = 4.1\%$ of the S burnt goes to SO₃, and 95.9% forms SO₂.

In order to secure the other information required, it is convenient to adopt the time bases indicated in the questions themselves.

2. *SO₂ leaving the burner in lb/hr.*

Basis: 1 hr of operation.

Lb S burnt	Lb pure S	Atoms S	Mols SO ₂	
680	0.994		0.959	$\frac{64.1}{32.1} = 1293 \text{ lb SO}_2 \text{ per hour}$
		32.1		

3. *Air consumption in cubic feet/minute.*

Basis: 1 min. Assume dry air and normal barometer.

Lb SO ₂	Mols SO ₂	Mols N ₂	Mols air	Cu ft at s.c.	
1293		79.9	100	359	$\frac{520}{492} = 743 \text{ cu ft air per minute}$
60	64.1	17.4	79		

The results of these calculations are shown in Fig. 6-2.

4. *Gases leaving burner and leaving cooler.*

Basis: 1 min.

Lb SO ₂	Mols SO ₂	Mols gas, including SO ₃	Cu ft at s.c.	
1293		100.74	359	$\frac{273 + 760}{273} = 2645 \text{ cu ft/min leaving burner}$
60	64.1	17.4		

The volume of the gas leaving the cooler is found by correcting that leaving the burner for the temperature drop from 760°C (1033°K) to 70°F (530°R).

$$\frac{\text{Cu ft at } 760^{\circ}\text{C}}{\text{At } 0^{\circ}\text{C, or } 32^{\circ}\text{F}} = \frac{2,645}{273} \times \frac{530}{492} = 753 \text{ cu ft/min leaving cooler}$$

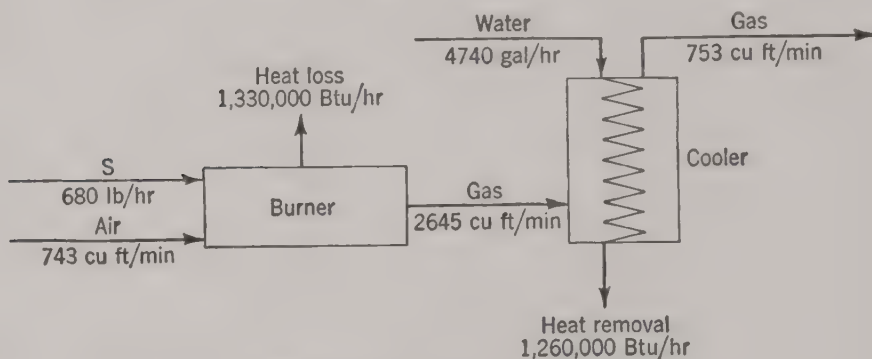


FIG. 6-2. Combustion of sulfur.

5. Heat dissipated from burner in Btu per hour.

Basis: 100 mols gas as analyzed = 100.74 mols total gas (including SO_3).

The heat evolved by formation of SO_2 and SO_3 in the burner is

$$(17.4)(70,920)(1.8) + (0.74)(93,900)(1.8) = 2,350,000 \text{ Btu}$$

The heat carried out of the burner by each gas is its number of mols times the difference between 1400°F (760°C) and 60°F, or 1340 Fahrenheit degrees, times the average specific heat between 1400°F and 60°F.

HEAT CONTENT OF GAS LEAVING BURNER

Gas	Mols	$M\bar{c}_{p,av}^{\circ}$ 60 to 1400°F	(Mols)($M\bar{c}_{p,av}^{\circ}$)(1340), Btu
SO_2	17.4	11.7	273,000
SO_3	0.74	17.0	17,000
O_2	2.7	7.8	28,000
N_2	79.9	7.3	781,000
Total.....	100.74		
Sensible heat remaining in gases.....			1,099,000

The heat dissipated in the burners is that evolved (2,350,000 Btu) less that carried out by the gases (1,099,000 Btu) = 1,151,000 Btu per 100 mols of gas as analyzed, or per $17.4 + 0.74 = 18.14$ atoms of S burnt.

Since the sulfur burnt per hour is $(680)(0.994)/32.1 = 21.0$ atoms, the heat dissipated per hour is

$$1,151,000 (21.0/18.14) = 1,330,000 \text{ Btu/hr}$$

6. *Water used in cooler in gallons per hour.*

Basis: 100 mols of gas as analyzed.

HEAT CONTENT OF GAS AT 70°F

Gas	Mols	$Mc_{p,av}^{\circ}$ 60 to 70°F	(Mols)($Mc_{p,av}^{\circ}$)(10), Btu
SO ₂	17.4	9.5	1650
SO ₃	0.74	12.0	89
O ₂	2.7	7.0	189
N ₂	79.9	7.0	5600
Total.....	100.74		
Sensible heat in gases.....			7528

The heat given up by the gases in passing through the cooler is

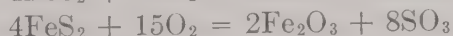
$$1,099,000 - 7528 = 1,091,000 \text{ Btu}$$

on a basis of 18.14 atoms of S burnt. Converting to an hourly basis, which corresponds to 21.0 atoms of S, gives

$$1,091,000(21.0/18.14) = 1,262,000 \text{ Btu}$$

as the heat removed from the gases or absorbed by the water. Since the cooling water rises 32 Fahrenheit degrees, the hourly requirement is $1,262,000/32 = 39,500$ lb, or 4740 gal, on the assumption that all heat lost by the gases is removed by the cooling water.

Combustion of pyrites. When gases produced from combustion of pyrites are analyzed it is discovered that there is an oxygen "disappearance" due not only to any SO₃ that may be formed but also to the oxygen consumed in forming Fe₂O₃, which is also a product of the combustion. In so far as the cinder is completely roasted to trivalent iron, this can be allowed for quantitatively by the relationships implied in the reactions



Unburnt sulfide and lower oxides of iron can be determined by analysis of a representative sample of the cinder and allowed for. From a furnace that is well designed and well operated, however, they should be small in amount. Allowance for sulfides of other metals can be based on the anal-

ysis of the pyrites. While the cinder usually holds relatively large quantities of sulfur, it should be in the form of adsorbed SO_3 (*i.e.*, basic sulfate). Since this is stoichiometrically equivalent to direct addition of SO_3 to the cinder, it does not affect the gas analyses or their quantitative interpretation, except that such SO_3 does not leave the furnace in the gas, and hence, to compute the SO_3 in the burner gas, this adsorbed SO_3 in the cinder must be subtracted from the total formed in the furnace, as indicated by the burner-gas analysis.

Thus, with 6.2% SO_2 and 12.1% O_2 in the average burner gas from a well-roasted pyrites, what percentage of the sulfur is oxidized to SO_3 in the burner? From the preceding equations, on the basis of 100 mols of gas as analyzed, the oxygen consumed to form SO_2 is evidently $11/8$ of 6.2, or 8.53 mols. Since the N_2 is 81.7, the O_2 from the air is 21.72 mols. Hence, O_2 unaccounted for is $21.72 - 12.1 - 8.53 = 1.09$, which is equivalent to $8/15$ of $1.09 = 0.58$ mol SO_3 . Hence, the total sulfur burnt is $6.2 + 0.58 = 6.78$ mols and the per cent oxidized to SO_3 is

$$(0.58/6.78)100 = 8.6\%$$

An analysis of the cinder would make it possible to tell how much of this left the burner in the gases.

Illustration 2. Pyrites fines are burnt in a Herreshoff burner to form SO_2 for conversion to SO_3 in a sulfuric acid plant. The pyrites used carry 48% S. Analysis of the burner gas shows 9.32% SO_2 and 6.93% O_2 . The cinder carries 2.15% S. What per cent of the sulfur fired leaves the burner as SO_3 in the burner gas?

Solution.

Basis: 100 mols of burner gas.

Gas	Mols	Mols O_2
SO_2	9.32	9.32
O_2	6.93	6.93
N_2	83.75	
Total.....	100.00	16.25
O_2 to iron in cinder, $\approx \text{SO}_2$ formation, $(3/8)9.32$		3.50
83.75(21/79).....		19.75 O_2 accounted for 22.27 O_2 from air
SO_3 formed, $(8/15)2.52$		2.52 O_2 disappearance 1.34 mols

This gives as the per cent of the total sulfur oxidized to SO_3 ,

$$100(1.34)/(9.32 + 1.34) = 12.56\%$$

leaving 87.44% as SO_2 .

Some of the SO_3 remains in the cinder as adsorbed SO_3 and the remainder goes into the burner gas. The analysis shows the percentage of sulfur in the cinder, and this can be converted to the equivalent percentage of SO_3 . First, however, the weight of the SO_3 -free cinder is computed. This is done as follows:

Basis: 100 lb pyrites.

The sulfur fired is 48 lb and the remainder, 52 lb, is gangue and iron together. The latter is all oxidized to Fe_2O_3 and the gangue is assumed to remain constant in weight. Regardless of whether the sulfur is oxidized to SO_2 or SO_3 , the equations for combustion of pyrites show that for each 8 atoms of S burnt 3 mols of O_2 combine with iron. Therefore, the increase in weight of the gangue and the iron as they appear in the cinder is

$$\begin{array}{c|c|c|c} \text{Lb S} & \text{Atoms S} & \text{Mols O}_2 & \\ \hline 48 & & 3 & 32 \\ \hline & 32.1 & 8 & \end{array} = 18.0 \text{ lb of O}_2$$

Hence, the weight of the SO_3 -free cinder is $52 + 18 = 70$ lb.

The sulfur in the cinder as adsorbed SO_3 is 2.15% of the weight of the cinder. If x be the number of pounds of sulfur in the cinder, then $(80/32)x$ is the corresponding weight of SO_3 in it and the total weight is $70 + (80/32)x$. From the condition that the percentage of sulfur is 2.15, there is obtained the equation,

$$\frac{100x}{70 + (80/32)x} = 2.15$$

This gives, for x , 1.59 lb of S which remain in the cinder as SO_3 . This is 3.31% of the 48 lb fired. Since 12.56% of the S fired was oxidized to SO_3 , $12.56 - 3.31 = 9.25\%$ left the burner as SO_3 .

Bisulfites. The formation of SO_3 is one of the factors that interfere with bisulfite manufacture. SO_3 may form in the burners as illustrated above and thus be present in the gas entering the absorbing apparatus, or it may form in the absorbers themselves. Another factor influencing the results is the kind of lime used. The amount of lime necessary to absorb a given amount of SO_2 gas will be different for one containing a high percentage of magnesia from what it will be for one consisting of nearly pure CaO , since the equivalent weights of lime and magnesia are not the same.

Illustration 3. The cooled gas of Illustration 1 is absorbed in a milk of lime, to form bisulfites, in a tower in which the absorbing solution flows countercurrent to the gas. The gas leaves the tower at 76°F , containing 2.8% O_2 and no SO_2 . The bisulfite liquor produced is 7.05% total SO_2 , of which 1.15% is "free," the rest, 5.90%, being present as

bisulfites. The dolomitic lime used is 82% CaO and 16% MgO. Calculate the following:

1. The volume of gas leaving the absorbing tower per minute
2. The consumption of lime per hour and the water necessary to slake it
3. The amount of bisulfite liquor produced per hour

Items 2 and 3 can, of course, be determined by actually measuring the quantities involved. On the other hand, the measurement of large quantities of flowing liquids requires the use of equipment that is not often available in connection with the process. The ratio of these different quantities to one another can be determined from their analyses. Since these analyses are easily carried out, they are very useful in computing the amounts in the various streams when the quantity of one of them is known (in this case the sulfur fed to the burners was weighed directly).

SUMMARY OF OTHER DATA AND CALCULATED QUANTITIES

Pounds S (99.4% pure) burnt per hour.....	680
Per cent of above burning to SO ₂	95.9
Air at 60°F used, cu ft/min.....	743
Analysis of SO ₃ -free burner gas:	
SO ₂	17.4%
O ₂	2.7%
Gas leaving cooler (entering absorber), cu ft/min.....	753
Temperature of gases leaving cooler.....	70°F

1. *Volume of gas leaving absorbing tower per minute.*

Basis: 1 min.

Cu ft air at 60°F	N ₂ at 60°F	Dry waste gas	
743	79	100	536
	100	(100 - 2.8)	520

= 623 cu ft/min dry gas at 76°F

It must, however, be remembered that this gas is practically saturated with water vapor. Since the vapor-pressure lowering of water in a saturated lime solution is negligible, the partial pressure of water vapor at 76°F is 0.87 in., whence the total volume is

$$623(29.92)/(29.92 - 0.87) = 642 \text{ cu ft/min}$$

2. *Consumption of lime and water per hour.* As a result of absorption of the sulfur oxides, calcium and magnesium sulfates, bisulfites, and free sulfurous acid are formed. First, it must be shown qualitatively whether any oxidation of SO₂ takes place in the absorber; and second, the amount of this oxidation must be calculated, since for every mol of SO₃ (from oxidation of SO₂) going to sulfate, 1 mol of lime or magnesia must be

used, whereas only 1 mol of the basic oxides is required for every 2 mols of SO_2 forming bisulfites.

There is available the analysis of the gas entering the tower and of that leaving it. Except for minor solubility effects in water and bisulfite liquor, the nitrogen in this gas is practically unchanged and is, therefore, a suitable basis for comparing the inlet and outlet gases.

Basis: 100 mols N_2 .

Component	Ratio to 100 mols N_2	
	At entrance	At exit
SO_2	$17.4/0.799 = 21.78$	None
O_2	$2.7/0.799 = 3.38$	$2.8/0.972 = 2.88$

Granting no oxidation, the ratio of oxygen to nitrogen should be the same at exit and entrance. However, there is a decrease of

$$3.38 - 2.88 = 0.50 \text{ mol O}_2$$

resulting from oxidation of SO_2 which takes place appreciably in dilute solution. This 0.50 mol O_2 oxidizes 1.00 mol of SO_2 . Of the total SO_2

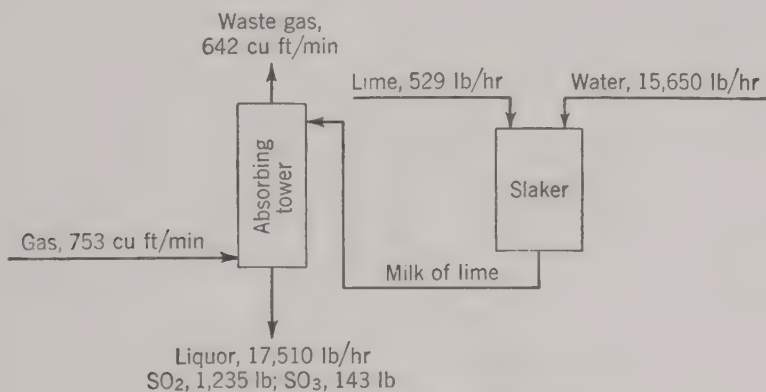


FIG. 6-3. Production of bisulfite liquor.

entering the tower, therefore, 1.00/21.78, or 4.6%, is oxidized to SO_3 . Since only 95.9% of the S burnt enters the absorber as SO_2 , the oxidation in the absorber is 4.4% of the sulfur burnt, which added to the 4.1% previously oxidized in the burners makes a total of 8.5% of all the sulfur burnt which goes to SO_3 . All this enters the absorber, since the air is dry, but had it contained moisture, some or all of the first 4.1% would have been condensed in the coolers as H_2SO_4 .

The amount of oxides necessary to absorb the SO_2 and SO_3 , respectively, can now be computed.

Basis: 1 hr.

Lb crude S	Lb pure S	Lb S in liquor as SO ₂	Mols SO ₂ in liquor	Mols combined SO ₂	
680	0.994	(1.0 - 0.085)	32.1	5.90	
				7.05	$\frac{7.05}{2} = 8.06 \text{ mols CaO + MgO}$
					per hour for the combined SO ₂ only

Lb crude S	Lb pure S	S as SO ₃	Mols SO ₃	
680	0.994	0.085	32.1	$\frac{0.085}{32.1} = 1.79 \text{ mols oxides for SO}_3$

Basis: 100 lb lime.

	Mols
CaO, 82/56.....	1.463
MgO, 16/40.3.....	0.397
Total oxides.....	1.860

Basis: 1 hr.

Lime required = (8.06 + 1.79) (100/1.86) = 529 lb/hour for combined SO₂ and SO₃

The amount of water used can be obtained by deducting from the total weight of the solution the weight of its components other than water. To compute the weight of the components in the liquor:

Lb crude S	Lb pure S	Lb S as SO ₂	
680	0.994	(1.0 - 0.085)	$\frac{64.1}{32.1} = 1235 \text{ lb SO}_2$
Lb crude S	Lb pure S	Lb S as SO ₃	
680	0.994	0.085	$\frac{80.1}{32.1} = 143 \text{ lb SO}_3$

	Pounds
Total weight of solids, 529 (lime) + 1235(SO ₂) + 143(SO ₃).....	1,907
Total weight liquor, 1235/0.0705.....	17,510

By difference, the water in the liquor is 17,510 - 1907 = 15,600 lb. To this must be added the water picked up by the gas, certainly small, but calculated as follows:

The pressure of water vapor at 76°F is 0.87 in.

Cu ft gas per hour	Cu ft H ₂ O vapor	Cu ft at s.c.	Mols H ₂ O	
642 × 60	0.87	492	18	$\frac{18}{359} = 51.5 \text{ lb H}_2\text{O vaporized per hour}$
	29.92	536	359	

The total water used is, therefore, 15,650 lb/hour (see Fig. 6-3).

3. *Weight of bisulfite liquor produced per hour.*

This was calculated above to be 17,510 lb.

Chamber acid. Besides the burner, a "chamber plant" consists of three principal units—the Glover tower, the chambers, and the Gay-Lussac tower. The SO_2 converted to H_2SO_4 in the Glover tower comprises about 15% of the total acid production of a chamber plant. Except for a few per cent that is oxidized in the Gay-Lussac tower, the balance of the conversion takes place in the chambers themselves. Besides production of H_2SO_4 , the Glover tower functions to concentrate dilute chamber acid that is circulated back to it to cool the hot burner gases, and also to liberate oxides of nitrogen from nitrous vitriol made by absorbing these oxides in acid circulated through the Gay-Lussac tower. Both the chamber acid and the nitrous vitriol are pumped to the top of the Glover tower, where, in counterflow to the hot burner gases, the sensible heat of the latter serves to liberate steam and nitrous oxides. It is, therefore, important in the understanding of the chamber process to know the quantities of various acid streams being produced in and circulated through the various units of the plant.

Owing to the corrosive character of sulfuric acid, its measurement when in flow may not be feasible unless special equipment is already installed for that purpose. It is usually measured directly only when necessary, or where measurement is a normal plant operation, such as measurement of production. The quantities of the various streams must, therefore, be obtained by calculation.

The performance of each unit of the plant is so interwoven with that of the other units that any analysis generally involves evaluation of the performance of the entire plant. The problem below illustrates the method by which the desired information can be found.

Illustration 4.

TABULATED DATA

Sulfur:		Chamber acid:	
Tons per day.....	6.70	Tons per day.....	5.50
Purity.....	99.4%	Gravity.....	52.6° Bé
Burner gas:		Nitrous vitriol:	
SO_2	7.90%	N_2O_3 content as per cent	
O_2	12.75%	NaNO_3	2.60
N_2	79.35%	Mixed nitrous vitriol and cham-	
Gas leaving Glover tower:		ber acid fed to Glover	
SO_2	6.90%	tower:	
O_2	12.40%	N_2O_3 content as per cent	
N_2	80.70%	NaNO_3	1.64
Glover-tower acid:		Air temperature:	
Tons per day.....	20.25	Dry bulb.....	57°F
Gravity.....	60.5° Bé	Wet bulb.....	51°F
		Barometer.....	29.45 in.

Calculate from these data

1. The sulfur efficiency, *i.e.*, efficiency of conversion of sulfur to sulfuric acid
2. The per cent of the total acid made in the Glover tower
3. The tons per day of chamber acid returned to the Glover tower for concentration
4. The tons per day of water evaporated in the Glover tower
5. The tons per day of water fed to the chambers, as steam or otherwise
6. The tons per day of Glover-tower acid circulated through the Gay-Lussac tower
7. The NaNO_3 content of the nitrous vitriol, expressed as per cent of the sulfur burnt

Solution.

1. *Sulfur efficiency.* The Glover and chamber acids have different strengths and must be converted to a common basis before adding the productions of each unit to get the plant output. Similarly, the sulfur input must be converted to the same basis before the efficiency can be figured. Accordingly, the quantities of these acids and the sulfur burnt will be converted to the equivalent of 100% H_2SO_4 , and all other acid quantities will, in general, be expressed as or converted to 100% H_2SO_4 , unless otherwise stated.

Basis: 24 hr.

Input:

$$6.70(0.994)(98/32) = 20.40 \text{ tons of } 100\% \text{ H}_2\text{SO}_4$$

Output:

$$\text{Glover acid } (60.5^\circ\text{Bé} = 78.55\% \text{ H}_2\text{SO}_4)$$

$$20.25(0.7855) = 15.90 \text{ tons } 100\% \text{ acid}$$

$$\text{Chamber acid } (52.6^\circ\text{Bé} = 66.03\% \text{ H}_2\text{SO}_4)$$

$$5.50(0.6603) = 3.63 \text{ tons } 100\% \text{ acid}$$

$$\text{Total production, } 15.90 + 3.63 = 19.53 \text{ tons}$$

Conversion efficiency:

$$(19.53/20.40)100 = 95.7\%$$

2. *Per cent of total acid made in Glover tower.*

Basis. 100 mols of burner gas as analyzed.

Gas	Mols	Mols O ₂
SO ₂	7.90	7.90
O ₂	12.75	12.75
N ₂	79.35	
Total.....	100.00	20.65 O ₂ accounted for
79.35(21/79).....		21.09 O ₂ from air
		0.44 O ₂ to SO ₃

SO₃, $(2/3)0.44 = 0.30$ mol

Total S burnt, $7.90 + 0.30 = 8.20$ atoms

S converted to H₂SO₄, $8.20(0.957) = 7.85$ atoms

The data that will show the amount of SO₂ converted to H₂SO₄ in the Glover tower are the compositions of the gases entering and leaving it. Assuming that the N₂ passes through unchanged, it can be made the basis of comparison. Using the same basis of 100 mols of burner gas, the mols of each component in the gas leaving the Glover tower is found by multiplying the percentage composition by the ratio of the nitrogen contents of the two gases, namely, by 79.35:80.70.

GAS LEAVING GLOVER TOWER

Gas	Per cent	Factor	Mols per 100 mols burner gas
SO ₂	6.90	79.35/80.70	6.78
O ₂	12.40	79.35/80.70	12.19
N ₂	80.70	79.35/80.70	79.35
Total.....	100.00	98.32

Comparison of the last column with the tabulation of the burner-gas data shows that the SO₂ decrease is $7.90 - 6.78 = 1.12$ mols and the oxygen decrease is $12.75 - 12.19 = 0.56$ mol, which checks the SO₂ figure. Since the total sulfur converted to H₂SO₄ is 7.85 atoms, the conversion taking place in the Glover tower amounts to $(1.12/7.85)100 = 14.3\%$. However, the SO₃ in the burner gas, which was found to be 0.30 mol, also condenses as H₂SO₄ in the Glover tower. This makes the total conversion in this tower $100(1.12 + 0.30)/7.85 = 18.1\%$ of the entire plant production. This value will be used in later calculations.

3. *Tons chamber acid returned to Glover tower for concentration.* Total production of the plant was calculated to be 19.53 tons. This gives $19.53(0.181) = 3.54$ tons that were made in the Glover tower. From this tower 15.90 tons were drawn off as product; the difference,

$$15.90 - 3.54 = 12.36 \text{ tons}$$

is chamber acid that was concentrated in the Glover tower.

In addition to the chamber acid, the Glover tower receives a quantity of nitrous vitriol from the Gay-Lussac tower. As is pointed out below, this acid may be considered to run through the Glover substantially unchanged with an equivalent quantity of Glover acid withdrawn for circulation to the Gay-Lussac. However, to the extent that any acid is actually formed from SO_2 in the Gay-Lussac, this acid must be considered to be a part of the 12.36 tons that is concentrated in the Glover tower by water evaporation.

4. *Water evaporated in Glover tower.* This is determined by a water balance. Input consists of water fed to the top of the tower in the form of mixed acid, made by mixing chamber acid with the nitrous vitriol from the Gay-Lussac tower, and of water vapor in the air used for combustion.

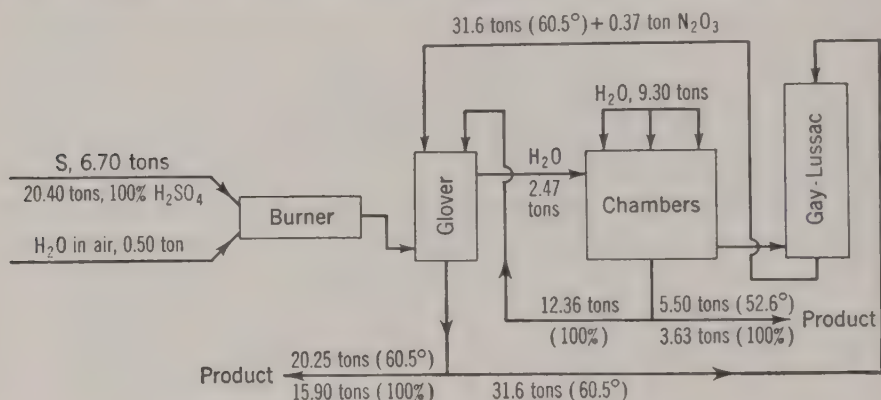


FIG. 6-4. Chamber-acid problem. Basis: 24 hr.

Water output includes water in the acid issuing from the bottom plus that evaporated. The latter passes from the top of the tower into the first chamber along with the other gases.

A simplification is made by assuming that no water is gained or lost by the H_2SO_4 circulated through the Gay-Lussac tower. A small quantity of acid mist and water is carried into this tower by the gases leaving the last chamber, but this is negligible compared with the quantity of acid passing through the tower. Water input to the top of the Glover tower due to the nitrous vitriol is then equal to water output in the acid from the bottom that is sent to the Gay-Lussac tower. Hence, water input may be treated as water brought in by the chamber acid plus water vapor in the burner gas (originally from the air); water output is that in Glover acid drawn off as product plus water evaporated.

From the dry-bulb temperature of 57°F and the wet-bulb temperature of 51°F , the humidity of the air is found from humidity tables¹ to be 66%. At 57°F the vapor pressure of water is 0.47 in., so that its partial pressure

¹ Or from Fig. A-3 (See Appendix).

in the air used is 0.31 in. The barometer is 29.45 in., whence the pressure of the dry air is $29.45 - 0.31 = 29.14$ in.

The water vapor entering the Glover tower as a result of the humidity of the air used for combustion is calculated as follows:

Tons crude S	Ton atoms S	Ton mols N ₂	Ton mols air	Ton mols H ₂ O	
6.70	0.994	79.35	100	0.31	$\frac{18}{29.14} = 0.50$ ton per day
	32.1	8.20	79	29.14	

The chamber acid contains 66.03% H₂SO₄, the rest being water, so that the amount of the latter entering the Glover tower from this source is $12.36(33.97/66.03) = 6.36$ tons. The total input of water, exclusive of that contained in the nitrous vitriol, is the sum of these two quantities, $6.36 + 0.50 = 6.86$ tons.

The water output in the form of Glover acid, exclusive of that returned to the Gay-Lussac tower, is

$$15.90(21.45/78.55) = 4.34 \text{ tons}$$

Consequently, the rest of the output, or $6.86 - 4.34 = 2.52$ tons, is evaporated by the hot burner gases.

5. *Water fed to the chambers.* With the exception of 0.50 ton of water entering with the air, the rest of the water in the product, both that combined with SO₃ to give H₂SO₄ and that used to give dilute acid, is added to the chambers.

The tons of water in the Glover and chamber acids above that necessary to make 100% H₂SO₄ are 4.34, as computed above, and

$$3.63(33.97/66.03) = 1.87 \text{ tons}$$

respectively. That combined with SO₃ to give H₂SO₄ amounts to $19.53(18/98) = 3.59$ tons. The water fed to the chambers is

$$4.34 + 1.87 + 3.59 - 0.50 = 9.30 \text{ tons per day}$$

6. *Tons Glover acid circulated to Gay-Lussac tower.* The analysis of the nitrous vitriol is given as equivalent to 2.60% NaNO₃. This is mixed with chamber acid before it is distributed to the top of the Glover tower. The mixed acid shows 1.64% NaNO₃. Consequently, the weight of the nitrous vitriol will be to the weight of the mixed acid inversely as the ratio of the equivalent NaNO₃ contents, or as 1.64:2.60. From this it is seen that the ratio of nitrous vitriol to chamber acid is 1.64:0.96. The actual weight of the chamber acid in the mixed acid is $12.36/0.6603 = 18.70$ tons, so that the weight of the nitrous vitriol is $18.70(1.64/0.96) = 32.0$ tons.

Part of this consists of the N₂O₃ content, *i.e.*,

$$(32.0)(0.0260)(38/85) = 0.37 \text{ ton}$$

leaving $32.0 - 0.37 = 31.6$ tons as the weight of 60.5°Bé Glover acid circulated through the Gay-Lussac tower. This is $31.6/20.25 = 1.56$ times the quantity of Glover acid drawn off as product.

7. NaNO_3 content of nitrous vitriol expressed as per cent of sulfur burnt. The equivalent NaNO_3 content of the nitrous vitriol is

$$32.0(0.0260) = 0.832 \text{ ton}$$

or, expressed as a percentage of the sulfur burnt,

$$(0.832/6.70)100 = 12.4\%$$

Contact conversion. If a contact converter for oxidation of SO_2 to SO_3 has an adequate amount of active catalyst, it should bring the outgoing gases to equilibrium concentrations for the reaction. While equilibrium is never fully achieved in industrial practice, it is sometimes approached sufficiently closely so that it is, in fact, the "bottleneck" that limits the performance of the equipment. Calculations based on the assumption that equilibrium is attained are a useful guide in design and a convenient standard against which to compare over-all plant performance. The classical equilibrium data of Bodenstein and Pohl on the reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$ are given by the following equation:¹

$$\log_{10} K = \frac{5186.5}{T} + 0.611 \log_{10} T - 6.7497$$

where $K = p_{\text{SO}_3}/p_{\text{SO}_2}p_{\text{O}_2}^{1/2}$, with partial pressures expressed in atmospheres. T is in degrees Kelvin. In order to avoid trial-and-error solution when temperature is unknown, the equation is presented graphically in Fig. 6-5.

The limitation that equilibrium imposes upon the combustion of SO_2 to SO_3 is analogous to that encountered in conversion of CO to CO_2 and H_2 to H_2O in a flame at high temperature (see Chap. 3). In the case of SO_2 oxidation, calculations are simplified by the fact that one has to consider only a single incomplete reaction instead of two simultaneously occurring reactions.

An important practical difference between the problems of temperature control of ordinary combustion flames on the one hand and of SO_2 conversion to SO_3 on the other is the fact that flames have a temperature range of some 1000 centigrade degrees throughout which fuel-reaction equilibria are favorable and uncatalyzed reaction rates are high, whereas for SO_2 oxidation the spread between the lowest temperature at which reaction rate reaches practicable values, even when using the best catalysts available, and temperatures at which equilibrium begins to block conversion seriously is only about 100 degrees. Under ordinary operating conditions the SO_2 oxidation reaction is too slow to "kindle" at tem-

¹ M. Bodenstein and W. Pohl, *Z. Elektrochem.*, **11**, 373 (1905).

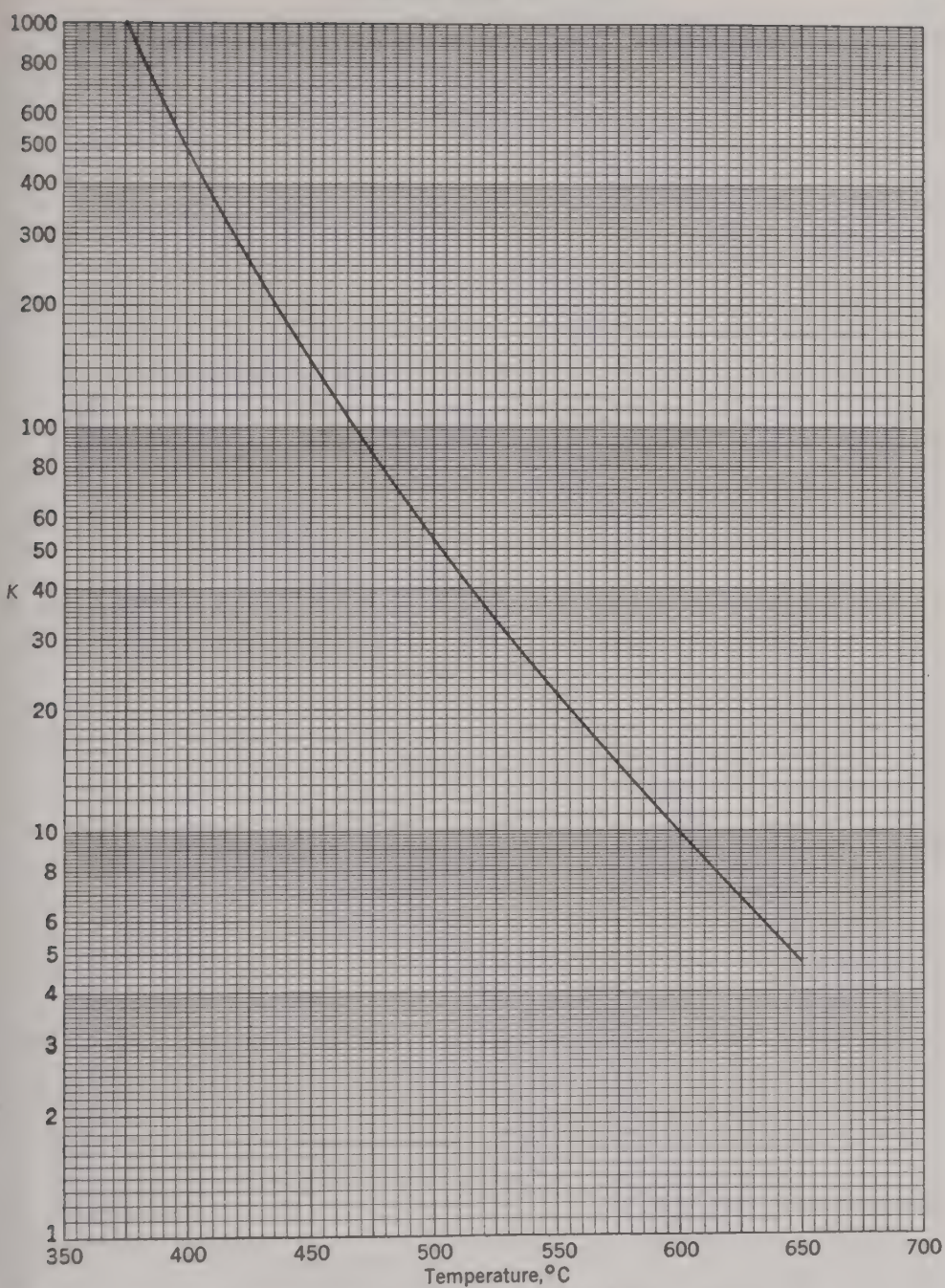


FIG. 6-5. Equilibrium constant for the reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$.
 $K = p_{\text{SO}_3} / p_{\text{SO}_2} p_{\text{O}_2}^{1/2}$. Partial pressures in atmospheres.

peratures much below 400°C, and it is usually advisable to have the reacting gases at about this temperature at the point where they enter the bed. Meanwhile, at 500°C the highest conversion of SO₂ to SO₃ attainable with air at normal pressures is about 96%. Even this can be secured only with very dilute gases; higher concentrations of initial SO₂ will depress the equilibrium conversion to nearly 90%. In short, the chemical reaction must be initiated at about 400°C and be completed at a level well below 500°C. Temperature control is a critical matter.

To compute the heat effects in a conversion operation requires knowledge of heat of reaction and heat capacities. These are functions of the temperature, but in the relatively narrow temperature range in question variations caused by temperature changes are not large. For purposes of initial orientation in the study of this and similar problems it is highly desirable to use average values. The following figures, corresponding to 450°C, will be used in the illustrations that follow:



$$M_{c_p} \text{ of SO}_2 = 12.2; \text{ of SO}_3 = 18.1; \text{ of O}_2 = 7.9; \text{ of N}_2 = 7.4$$

Illustration 5. A contact sulfuric acid plant is to operate on a cooled, scrubbed, and filtered gas containing 12% SO₂, 8% O₂, and 80% N₂. Each converter is to be a simple adiabatic reactor, provided with a supply of catalyst adequate to bring the gases leaving the converter substantially to equilibrium at their exit temperature. If the first reactor is to convert 60% of the SO₂ in the inlet gas to SO₃, to what temperature must the inlet gas be preheated and at what temperature will the gases leave the converter?

Solution. The fact that the inlet gas composition is known and a given conversion has been agreed upon fixes the composition of the exit gas, which in turn establishes the exit temperature, as a result of the relation between composition and temperature under the equilibrium conditions existing at the exit. In the light of the given inlet-gas analysis, the fixed exit-gas composition fixes the amount of chemical reaction and hence the reaction heat liberated per unit of total gas throughout. In an adiabatic reactor, this heat goes solely to raise the temperature of the gases. Since the exit temperature is known, the corresponding inlet temperature is easily determined by an energy balance.

Basis: 100 g mols of inlet gas.

<i>Exit gas</i>	<i>Mols</i>
SO ₃ , 12(0.60).....	7.20
SO ₂ , 12 - 7.20.....	4.80
O ₂ , 8 - 0.5(7.20).....	4.40
N ₂	80.00
Total.....	96.40

If one assumes that the total pressure is substantially atmospheric, mol fractions are numerically equal to partial pressures in atmospheres and $K = (7.20/96.40)/(4.80/96.40)(4.40/96.40)^{1/2} = 7.00$. From Fig. 6-5, the exit temperature is 624°C.

The energy balance can now be written as follows, letting t = the unknown inlet temperature in degrees centigrade:

$$22,650(7.20) = [(7.20)(18.1) + (4.80)(12.2) + (4.40)(7.9) + (80.0)(7.4)](624 - t)$$

Solving, $t = 424^\circ\text{C}$.

Illustration 6. The catalyst to be used in the converter of Illustration 5 is sufficiently active to ignite the reaction satisfactorily at 400°C . It is proposed to take advantage of this activity by reducing the preheat temperature of the inlet gases from 424°C to 400°C . If this is done and the reaction goes substantially to equilibrium, as before, what per cent conversion of SO_2 to SO_3 will it be possible to obtain in the reactor?

Solution. Since the conversion is unknown, the material balance on the operation is not yet fixed, and it is difficult to avoid trial-and-error methods. One possibility is to assume a conversion, calculate the exit temperature by means of an energy balance, and then check to see if the equilibrium constant read from Fig. 6-5 agrees with that computed from the assumed conversion. The process can then be repeated until the two values of K agree. Another possibility is to assume an exit temperature, read K from Fig. 6-5, calculate the corresponding conversion, then check to see if an energy balance is satisfied. Either method is workable, but as soon as one sets up an equation relating the conversion and K , it is seen that it is a little easier to calculate K from the conversion than the conversion from K . For this reason, the first of the two methods described is simpler to work out and will be adopted. For the first trial, choose a conversion of 65% (a figure somewhat higher than the 60% of Illustration 5 because of the more favorable temperature conditions) and set up the material balance on the converter.

Basis: 100 g mols of inlet gas.

<i>Exit gas</i>	<i>Mols</i>
SO_3 , 12(0.65).....	7.80
SO_2 , 12 - 7.80.....	4.20
O_2 , 8 - 0.5(7.80).....	4.10
N_2	80.00
Total.....	96.10

Let t = the exit temperature in degrees centigrade. By an energy balance,

$$\begin{aligned}
 &7.80(22,650) \\
 &= (t - 400)[7.80(18.1) + 4.20(12.2) + 4.10(7.9) + 80.00(7.4)] \\
 &= 816(t - 400)
 \end{aligned}$$

Solving, $t = 617^\circ\text{C}$.

At 617°C , the value of $p_{\text{SO}_3}/p_{\text{SO}_2}p_{\text{O}_2}^{1/2}$ at equilibrium (read from Fig. 6-5) is 7.8, while the value corresponding to the assumed conversion is $(7.80)/(4.20)(4.10/96.10)^{1/2} = 9.0$. Evidently, the assumption of 65% conversion is too high, and the answer must lie between 60% and 65%. Successive trials lead to a substantial check at an exit temperature of 612°C and a conversion of 63.6%. These trials do not require new calculations of the heat capacity of the products of reaction, since little error is introduced by assuming that the heat capacity of the product gases is substantially equal to the value of $816 \text{ cal}/^\circ\text{C}$, as computed above. The only change in heat capacity is due to the reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$; and this has negligible effect on the heat capacity of the mixture, because the heat capacity of SO_3 is not much different from that of $\text{SO}_2 + \frac{1}{2}\text{O}_2$, and in any case the mols affected by reaction are small compared to the total number of mols in the mixture.

Illustration 7. A contact sulfuric acid plant has two simple adiabatic converters connected in series. In order for the reaction to kindle properly, the gases must enter each converter at not less than 400°C . The gas lines to each converter are equipped with heat exchangers adequate to bring the gases to the desired temperature, by heating or cooling as the situation may require. The quantity of catalyst is sufficient to bring the gases passing through each converter to substantial chemical equilibrium, but the resistance to gas flow is such that not over 200 pound mols of gas per hour can be put through either converter. Moreover, plant conditions elsewhere require that the original gases going to the converter system contain 12% SO_2 , 8% O_2 , and 80% N_2 . Under these conditions, what per cent conversion can be realized? In order to increase the conversion to 97%, it has been proposed to recycle part of the gases from the outlet of the second converter back to the inlet of this converter, otherwise keeping unchanged all conditions as described above. With this arrangement, what is the maximum capacity of the converter system, in terms of pound mols of SO_3 produced per hour?

Solution. This plant is typical of many installations in the chemical industry, in that it is sufficiently flexible to permit a number of different sets of operating conditions. It is the responsibility of the engineer in charge to recommend the particular operating conditions most desirable from an economic standpoint. If one considers first the case without recycle, the inlet temperature to each converter is evidently within the control of the operator with the sole limitation that it must be at least 400°C . From an economic point of view, it is obvious that, other things

being equal, the inlet temperatures should be adjusted in such a way as to cause the maximum possible conversion of SO_2 to SO_3 . In this case, the lower the temperature, the more favorable the equilibrium, and therefore the best inlet temperature for each converter is the lowest one compatible with proper kindling, *i.e.*, 400°C . Another way of stating the situation is to say that the conversion obtainable in the converter system as a whole depends upon the amount of heat that can be removed between the point where the gases enter the converter system and the point where they leave. Maximum removal of heat is obtained when the exchanger preceding each converter cools the inlet gas stream to the lowest possible temperature, which is 400°C .

With an inlet temperature of 400°C , the first of the two converters is identical with the reactor of Illustration 6. Therefore, the exit gases from the first converter leave at 612°C , and on a basis of 100 g mols of inlet gas contain 7.65 mols of SO_3 , 4.35 mols of SO_2 , 4.17 mols of O_2 , and 80.00 mols of N_2 , or a total of 96.17 mols. These gases enter the second converter at 400°C , and the composition and temperature of the gases leaving the second converter may be calculated by a trial-and-error solution of exactly the same type as demonstrated in Illustration 6.

Assume an over-all conversion of SO_2 in the converter system of 90 per cent.

Basis: 100 g mols of inlet gas to first converter.

<i>Exit gas from second converter</i>	<i>Mols</i>
SO_3 , 12(0.90).....	10.80
SO_2 , 12 - 10.80.....	1.20
O_2 , 8 - 0.5(10.8).....	2.60
N_2	80.00
Total.....	94.60

Let t = the exit temperature from the second converter. Then

$$\begin{aligned} & (10.80 - 7.65)(22,650) \\ &= (t - 400)[(10.80)(18.1) + (1.20)(12.2) + (2.60)(7.9) + 80.0(7.4)] \\ & \qquad \qquad \qquad = 823(t - 400) \end{aligned}$$

Solving, $t = 487^\circ\text{C}$. From the assumed conversion,

$$p_{\text{SO}_3}/p_{\text{SO}_2}p_{\text{O}_2}^{1/2} = 10.80/(1.20)(2.60/94.60)^{1/2} = 54$$

From Fig. 6-5, $p_{\text{SO}_3}/p_{\text{SO}_2}p_{\text{O}_2}^{1/2} = 70$. The first trial is therefore too low. Succeeding trials lead to a check at an over-all conversion of 91% and an exit temperature of 490°C . The corresponding analysis of the gas leaving the second converter is 11.58% SO_3 , 1.14% SO_2 , 2.68% O_2 , and 84.60% N_2 .

The results of the calculations show that the use of two simple adiabatic converters in series increases the over-all conversion of SO_2 to SO_3 in the

converter section of the plant from about 64% to 91%. However, even 91% is too low a figure to be considered for a practical operation. Most of the unconverted SO_2 in the gases leaving the converter system passes through the absorption towers without being absorbed and is lost in the waste gases from the absorbers. If SO_2 lost in this manner amounts to 9% of the input to the converter system, it is not only an economic waste of major proportions but also a nuisance that would not be tolerated by most local political authorities. It is imperative to increase the conversion by some means, such as, *e.g.*, the installation of additional adiabatic converters in series, substitution of converters with internal cooling coils for the present adiabatic type, or provision for some kind of recycle arrangement, along the lines of the one that has been proposed.

By the same reasoning employed in discussion of the setup with two simple adiabatic reactors in series, it follows that the best way to operate the system with recycle on the second converter is to fix the inlet temperature to each converter at 400°C . If this is done, the first of the two converters is again identical with the converter in Illustration 6, and therefore, on a basis of any convenient amount of inlet gas, the amount and composition of the gases leaving the first converter are known. As for the second converter, the composition of the exit gases is fixed by the fact that the recycle and product gases withdrawn from the converter system must have the same composition, together with the knowledge that the latter analysis corresponds to 97% conversion of SO_2 to SO_3 .

Basis: 100 g mols of inlet gas to first converter.

<i>Product from converter system</i>	<i>Mols</i>
SO_2 , 12(0.03).....	0.36
SO_3 , 12 - 0.36.....	11.64
O_2 , 8 - 0.5(11.64).....	2.18
N_2	80.00
Total.....	94.18

The exit temperature from the second converter corresponds to equilibrium at 97% conversion: $p_{\text{SO}_3}/p_{\text{SO}_2}p_{\text{O}_2}^{1/2} = 11.64/(0.36)(2.18/94.18)^{1/2} = 212$. From Fig. 6-5, the exit temperature is 433°C . The amount of recycle can be determined by means of an energy balance on the second reactor. On the same basis as above, let x = the number of gram mols of recycle. The heat capacity of the product stream is

$$(0.36)(12.2) + (11.64)(18.1) + (2.18)(7.9) + (80.00)(7.4) = 824 \text{ cal}/^\circ\text{C}$$

and that of the recycle is $824x/94.18 = 8.74x$, in the same units. SO_3 formed in the second reactor is $11.64 - 7.65 = 3.99$ mols. The energy balance follows:

$$(3.99)(22,650) = (433 - 400)(824 + 8.74x)$$

From this equation, $x = 219$ mols, and the total feed to the second converter is $219 + 96 = 315$ mols. The material balance of the process is thus complete, on a basis of 100 g mols of inlet gas to the converter system.

According to the statement of the situation in the plant, the maximum flow of gas at any point is limited to 200 lb mols per hour. Clearly, the "bottleneck" so far as flow of gases is concerned occurs at the inlet to the second converter, and it is at this point that the limitation applies. Therefore, the production of SO_3 in pound mols per hour is to 200 as 11.64 (the production on a basis of 100 g mols of inlet gas to the converter system) is to 315. Using this proportion, one finds that the maximum capacity of the proposed recycle arrangement is 7.4 lb mols of SO_3 per hour.

It will be noted that the production with two adiabatic converters in series and no recycle is $200(0.12)(0.91) = 21.8$ lb mols of SO_3 per hour. In other words, recycle on the second reactor achieves the desired conversion at the expense of a very large reduction in plant capacity. One would be well advised to look into the possibility of other steps, perhaps other methods of recycle, which might lead to the desired increase in conversion without such a drastic reduction of capacity. An alternative frequently employed in practice is to dilute the inlet gas with air. The heat capacity of the additional air tends to depress the temperature rise accompanying a given conversion. Thus, at the expense of having to handle the additional air, the conversion attainable in each reactor can be increased. Recycle is equivalent to dilution with air, in its effect on a converter, and it has the distinct advantage of avoiding an increase in the quantity of gas that must be handled in other parts of the system—an increase which dilution with air entails.

Absorption of SO_3 . In the contact process, the system for recovering SO_3 from the converter gases by absorption not only is capable of manufacturing strong sulfuric acid but can be adapted, if desired, to produce oleum (fuming sulfuric acid) in amounts and strengths that can be varied to suit the demand. While flexibility is thus a characteristic of systems for absorbing SO_3 , there are also definite limits on the possible range of operating conditions. These limitations arise chiefly from the relatively large heat effects accompanying the absorption of SO_3 , together with the effect of temperature on the capacity of sulfuric acid and oleum to absorb additional trioxide. It follows that stoichiometric calculations can be of considerable aid in the attempt to take full advantage of the flexibility of the system, as new conditions arise.

In material-balance calculations, which are a necessary preliminary to considering relations of energy and equilibrium in an SO_3 absorption tower, a minor complication is the variety of ways in which analyses of fuming sulfuric acid may be reported. In the laboratory, the analysis is

usually carried out by diluting the sample with water and titrating with alkali. Any free SO_3 in the original sample is, therefore, converted to H_2SO_4 before titration; and the alkali consumed is equivalent to the H_2SO_4 in the original sample plus the H_2SO_4 produced by reaction of free SO_3 in the original sample with the water of dilution. A frequent practice is to report the result of the titration as weight per cent H_2SO_4 , *i.e.*, 100 times the weight of H_2SO_4 equivalent to the alkali used, divided by

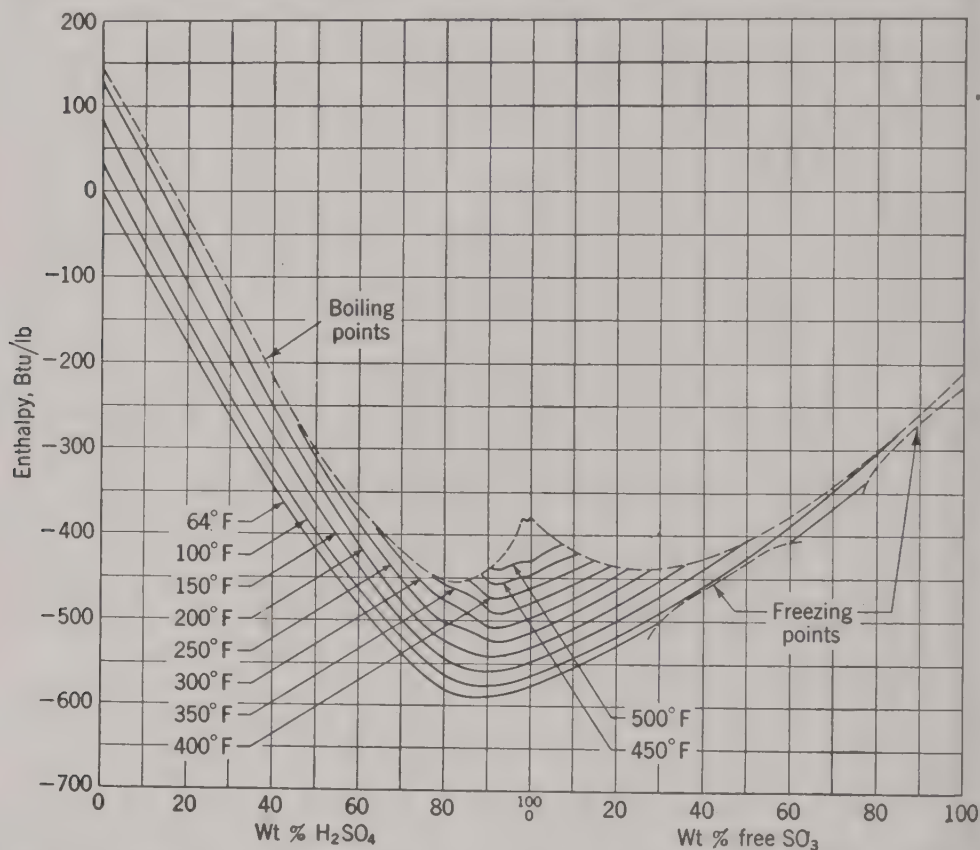


FIG. 6-6. Enthalpy-concentration diagram for sulfuric acid and oleum. Basis: Enthalpy for liquid water and SO_3 vapor = 0 at 64°F .

the weight of the original sample. Clearly, if there is any free SO_3 in the sample, the weight per cent H_2SO_4 will be greater than 100. While the chemist will often report his results in the above terms, it has long been the custom to market oleum on the basis of its strength expressed as weight per cent of free SO_3 . The plant engineer, who is under the necessity of dealing with both the laboratory and the sales organization, must be able to convert freely from one basis to the other. Perhaps the easiest way to do this is to keep in mind the fact that, if the per cent H_2SO_4 is greater than 100, the excess over 100 is the weight of water that combined with the free SO_3 in the original oleum as a result of dilution before titrat-

ing. The weight of this water, when multiplied by the ratio of the molecular weight of SO_3 to the molecular weight of H_2O , gives the weight of free SO_3 in the original sample, or, since the analysis is on a basis of 100 weight units of the sample, it gives the per cent free SO_3 . For example, the per cent free SO_3 corresponding to 104.7% H_2SO_4 is $4.7(80/18) = 20.9$. A third method, which is sometimes used to express the strength of fuming sulfuric acid, is to report the weight per cent of SO_3 , including both free SO_3 and that combined as H_2SO_4 .

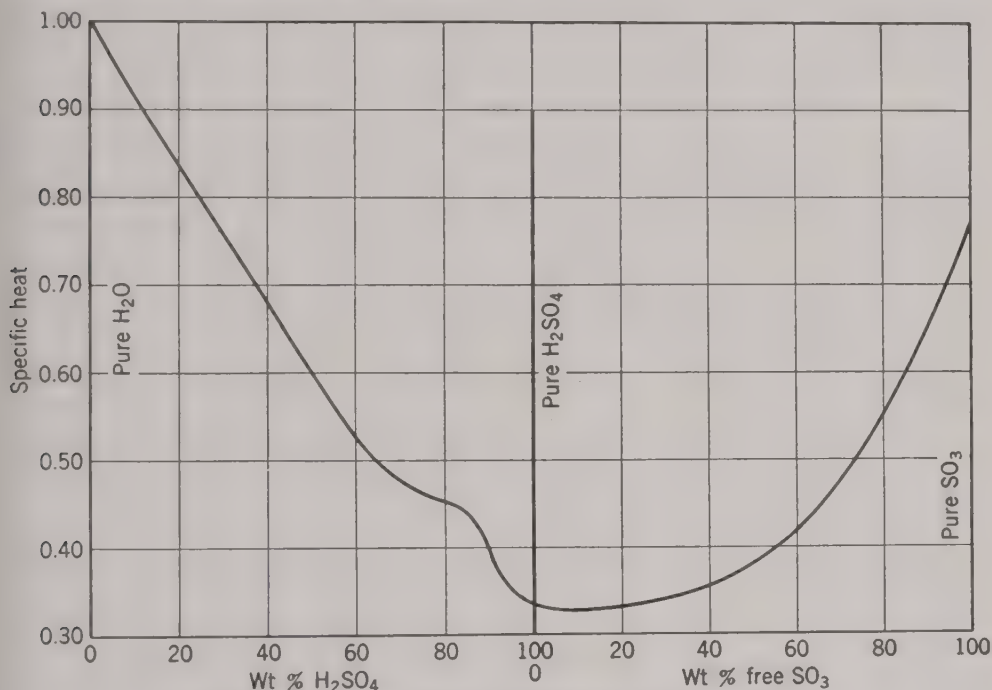


FIG. 6-7. Specific heats of mixtures of SO_3 and H_2O .

The heat content of sulfuric acid and oleum at various strengths and temperatures can be computed from basic data on heats of mixing and specific heats that are available in the literature. The results of a large number of calculations of this sort are conveniently presented in the form of an enthalpy-concentration diagram, Fig. 6-6.* In some situations, it is helpful to have specific heats as well. The data of Biron¹ on aqueous solutions of sulfuric acid at 20°C and of Knietzsch² on oleums at 30°C are presented in Fig. 6-7.

To determine the capacity of any given solution to absorb SO_3 one must know the vapor-liquid equilibrium. The absorbent is liquid H_2SO_4 . The problem is simplified by the fact that this has almost neg-

* D. B. Broughton, *Chem. Met. Eng.*, **52**, 123 (1945).

¹ See A. S. Socolik, *Z. physik. Chem. (A)* **158**, 305 (1932).

² R. Knietzsch, *Ber.*, **34**, 4069 (1901).

ligible volatility over the temperature ranges involved, but there still remain two independent variables, temperature and SO_3 concentration. Moreover, the equilibrium partial pressure P of SO_3 in the gas phase varies over very wide ranges under operating conditions. One can plot P against one of the independent variables for constant values of the other, but scales are awkward and interpolation clumsy. A more convenient correlation of the relationships is desirable.

The ideal-solution law, $P = P_0x$, where P_0 is the vapor pressure of the pure solute, SO_3 , at the temperature in question and x its mol fraction in the solution, should be tested, despite the fact that it is so generally honored in the breach. The most superficial inspection of the data¹ shows that the deviations are very great, but one should remember that the fractional deviations, P/P_0x , while often changing greatly with concentration, at a given concentration usually change relatively little with temperature. Plotting P/P_0x against x for various temperatures gives closely grouped curves. Because in the industry oleum concentrations are usually expressed in weight per cent, for convenience these curves are here plotted as P/P_0w against w , where w = weight fraction of free SO_3 in the solution. Since it was found that these curves were offset horizontally from each other by an amount practically proportional to the differences in temperature between them, they were reduced to the single curve² of Fig. 6-8. P_0 is given in Fig. 6-8 as a function of temperature. In the industrially important temperature range of 20 to 80°C, these curves probably deviate from the data little if any more than the experimental uncertainties of the data themselves.

Illustration 8. A contact sulfuric acid plant burning sulfur makes 98% acid as its main product. However, it has an outlet for a relatively small amount of 20% oleum. It makes this oleum by using an idle outdoor SO_3 -absorption tower, 7 ft in diameter by 30 ft high, supported on piers 5 ft high. This tower is packed with 20 ft of 3.25- by 3-in. "cyclo-helix" double spirals, surmounted by a thin layer of 1-in. Raschig rings and another of flint pebbles. Through this tower there is by-passed a small amount of converter gases, the gases leaving the top returning to the gas stream flowing into the main absorbers for the 98% acid. Oleum is recirculated by a pump to the top of the tower through an external liquid cooler. The oleum stream from the tower bottom is split; one part is withdrawn for product, and the other is diluted with the 98% acid before recycling. It is found impracticable to hold the concentration of the withdrawn oleum at exactly the 20% level required in the product. Consequently, the tower is operated to produce a stronger oleum, and

¹ F. D. Miles, H. Niblock, and G. L. Wilson, *Trans. Faraday Soc.*, **36**, 345 (1940).

² In the range below an abscissa of 0.1, data are limited and points scatter badly, as indicated by the dotted line.

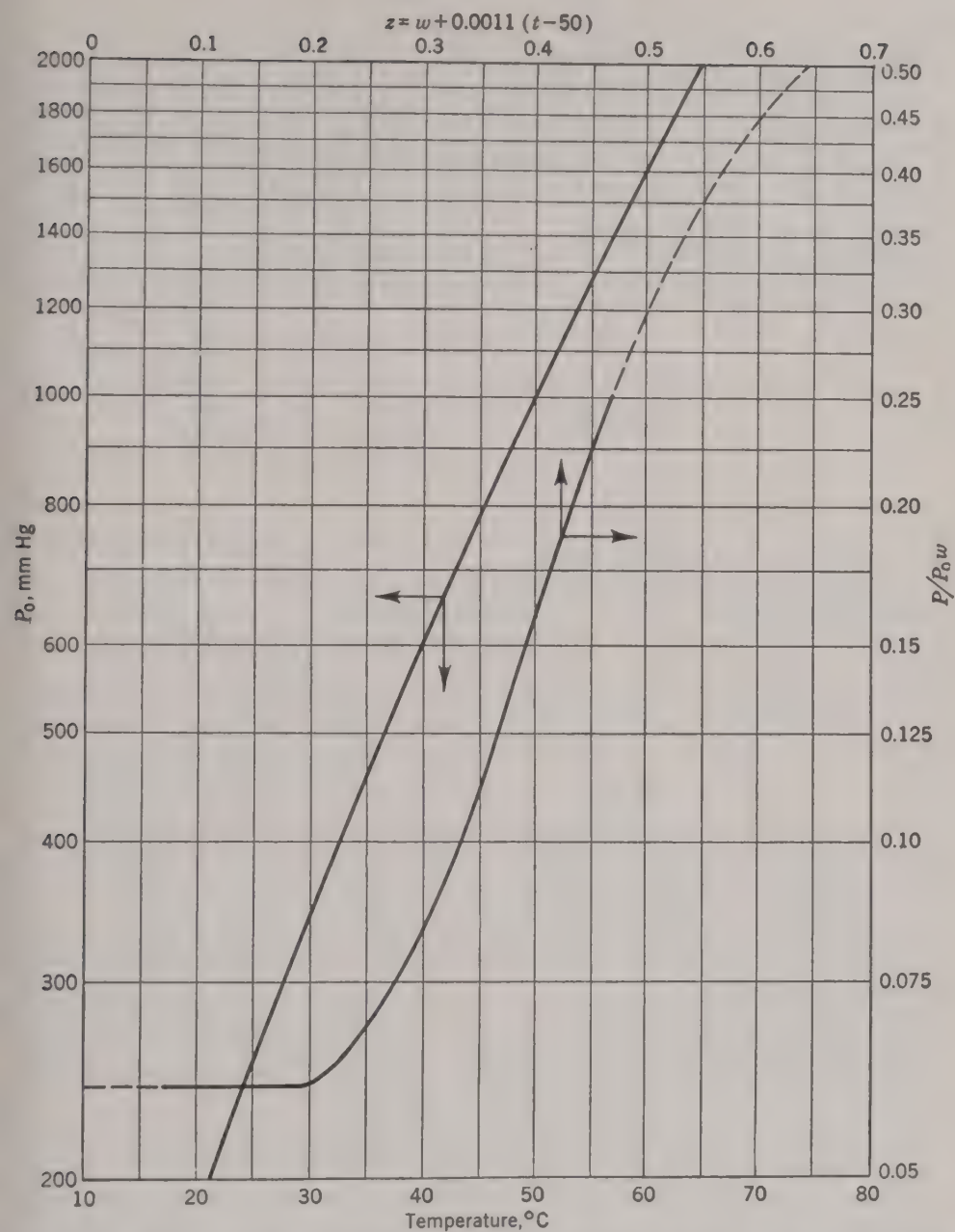


FIG. 6-8. Vapor pressure of oleum. P_0 = vapor pressure of pure SO_3 at t , P = vapor pressure of SO_3 over solution at t , w = weight fraction of SO_3 in solution, t = temperature, °C.

this is then diluted to 20% under controlled conditions in a separate operation. The daily (24-hr) production of 20% oleum is 28,800 lb.

The following are the present operating conditions: Oleum enters the top of the tower at 128°F containing 23.0% SO_3 . It leaves at the bottom at 122°F with 26.0% SO_3 . Make-up 98% acid enters the system at 80°F. Gas enters at 316°F with 9.9% SO_3 and leaves at 123°F with 1.7% SO_3 .

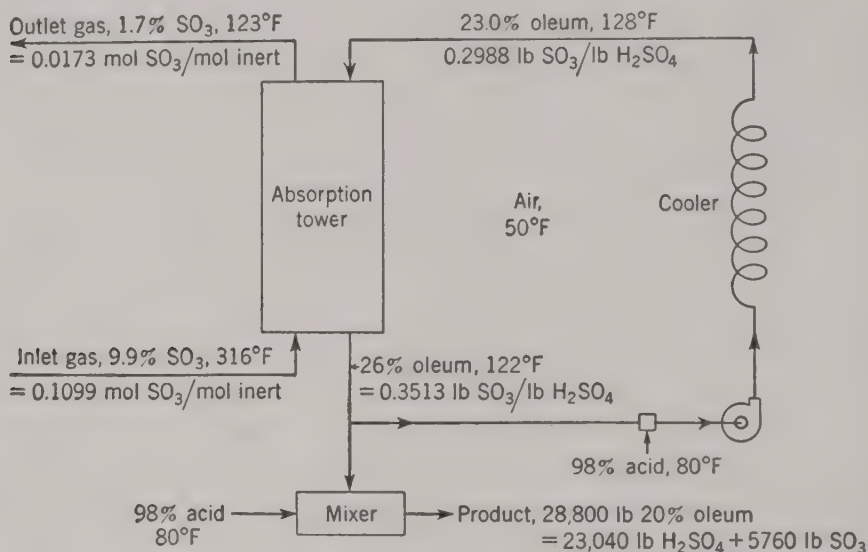


FIG. 6-9. Oleum tower of Illustration 8. Basis: 24 hr.

The ambient air is 50°F. The absolute pressure of the inlet gas is 820 mm Hg and at outlet, 810 mm.

1. Develop the material-balance relationships in the system.
2. What is the total heat release (heat lost to the surroundings) in the absorption system?
3. Determine the amount of heat being removed from the oleum flowing through the water cooler to the top of the tower.
4. Determine the heat lost from the tower itself.
5. Develop the gas-liquid equilibrium relations in the unit.
6. The plant manager wants to know if it is possible to adjust operating conditions so as to obtain oleum in approximately the same amount as at present but having a strength of 30% SO_3 instead of 26%. What is your opinion?

Solution.

1. *Material balances.* Figure 6-9 gives the framework for the material-balance picture (24-hr basis). The SO_3 picked up from the gas stream is enough to produce 28,800 lb of 20% oleum from 98% acid. Part of this SO_3 goes to form the 72 mols of free SO_3 in the product, but part is con-

sumed in converting the water in the 98% acid to H_2SO_4 . The 98% acid consumed can be determined by a hydrogen balance, which is perhaps more conveniently thought of as a total water balance, since the hydrogen in the product comes from no other source than total water. Now, 100 lb of 98% acid is 98 lb or 1 mol of H_2SO_4 plus 2 lb or 0.111 mol of H_2O or 1.111 mols total water (including that combined as acid); *i.e.*, 100 lb of 98% acid will react with SO_3 to produce $1.111(98) = 108.9$ lb of total pure H_2SO_4 . Hence the total 98% acid needed to produce 23,040 lb H_2SO_4 in the final product is $23,040/108.9 = 21,130$ lb. Of this, 2% is water, amounting to 23.9 mols, requiring the same number of mols of SO_3 to convert it to H_2SO_4 . Hence the total SO_3 absorbed from the gas stream is $72 + 23.9 = 95.9$ mols = 7670 lb. Total inert gas is

$$95.9/(0.1099 - 0.0173) = 1035 \text{ mols}$$

and the total bottom gas is $1035/0.901 = 1149$ mols. The weight of H_2SO_4 flowing down the tower is $7670/(0.3513 - 0.2987) = 146,300$ lb. The total liquid entering the top is $146,300/0.77 = 189,980$ lb and leaving the bottom is this plus the SO_3 absorbed, 197,650 lb. By simultaneous balances around the point of mixing of the bottom oleum with 98% acid to produce the 28,800 lb of product, one finds that 4960 lb of 98% acid are used at that point. The rest of this acid, 16,170 lb, enters ahead of the oleum recycle pump.

The degree to which the tower is idling is indicated by the fact that the superficial gas velocity entering the bottom is only 0.18 ft/sec and the liquid velocity entering the top is less than 2 ft/hr.

2. *Heat loss to surroundings.* From an over-all point of view, this absorption system itself is dissolving 95.9 mols of SO_3 in 16,170 lb of 98% acid to make 23,840 lb of 26% oleum, while at the same time 18.1 mols of excess SO_3 and 1035 mols of inert gas flow through unabsorbed. The thermal data for the following table are from Figs. 1-3 and 6-6:

OVER-ALL HEAT BALANCE
Basis: 24 hr. Base temperature, 64°F.
Heat quantities in thousands of Btu

Stream gases		Input	Output
SO_3 in.....	114(316 - 64)(13.3)	382	
SO_3 out.....	18.1(123 - 64)(12.2)	13
Inerts in.....	1035(316 - 64)(7.0)	1826	
Inerts out.....	1035(123 - 64)(6.9)	421
98% acid.....	16,170(-576)	-9320	
Oleum.....	23,840(-494)	-11,770
Heat loss, by difference.....		4,224

The total heat lost to the surroundings is 4,224,000 Btu per 24 hr. This is only 176,000 Btu per hour, which is very small, although it amounts to 177 Btu per pound of oleum produced.

3. *Heat removed in cooler.* The oleum flowing through the water cooler is 189,980 lb, made up of 16,200 lb of 98 % acid and, by difference, 173,780 lb of recycled 26 % oleum. Figure 6-6 is the basis of the following table:

HEAT BALANCE ON COOLER

Concentration	Temp., °F	Pounds	Enthalpy, Btu/lb	Enthalpy of stream	
				In	Out
26 % oleum	122	173,810	-494	-85,850,000	-95,200,000
23 % oleum	128	189,980	-501	
98 % acid	80	16,170	-576	-9,320,000	
Heat loss, by difference	+30,000

The striking thing is the inconsequential amount of heat lost by the acid, despite the mixing. There is, of course, a sensible-heat effect due to the rise in temperature of the liquids of a little over 600,000 Btu (from Fig. 6-7) which would have been evolved in addition to the 30,000 Btu had the liquids entered and left the cooler at the same temperature. The point is that the large numerical values of the enthalpies of Fig. 6-6 are due mainly to three effects: heat of condensation of SO_3 vapor, heat of combination of SO_3 with water to form H_2SO_4 , and heat of dilution of H_2SO_4 with water (doubtless also due to combination of some sort). In the case of mixing of 98 % acid with 26 % oleum, no condensation of SO_3 is taking place and heat effects involving water are small because of the small amount of water in 98 % acid.

The very great convenience of a data plot such as Fig. 6-6 is to a degree counterbalanced by its lack of precision when it is used in narrow areas, due to the fact that it involves the use of small differences between large numbers. Where proper data are available the problem can be met in many ways, as by enlarging the scale of a specific area or constructing an equivalent plot of data applicable only to that area.

4. *Heat loss from tower.* The first glance at the heat data on the tower shows that the heat losses from the walls exceed the heat release in it, because both streams leaving the tower are colder than either stream entering it. The magnitude of the losses from the tower can be determined by difference (the losses from the system as a whole, computed in Part 2, minus the losses from the cooler, calculated in Part 3) or by a balance around the tower itself. By the former method the losses amount to $4,224,000 - 30,000 = 4,184,000$ Btu per day. As is shown in the table below, a balance around the tower gives approximately the same result.

HEAT BALANCE ON TOWER
 Basis: 24 hr. Base temperature, 64°F.
 Heat quantities in thousands of Btu

Stream		Input	Output
Oleum	189,980(−501)	−95,200	
	197,620(−494)	−97,600
SO ₃	114(316 − 64)13.3	+382	
	18.1(123 − 64)(12.2)	+13
Inerts (assumed N ₂)	1035(316 − 64)(7.0)	+1,826	
	1035(123 − 64)(6.9)	+421
Heat loss by radiation, etc., by difference	+4,174
Total		−92,992	−92,992

This heat loss is about 3.3 Btu/(sq ft of tower surface)(hr)(°F temperature difference), which, while not excessive, is high enough to indicate at least a good wind or perhaps even rain at the time the data were collected.

The low bottom-liquid temperature relative to the hot entering gas is hard to explain. The heat capacity of the bottom-liquid stream from Fig. 6-7 is 65,600, compared with about 9000 for the gases. This (from Chap. 3) tends to drive the heat out in the bottom liquid. The tower is clearly coolest in the middle, and entering gas may by-pass outflowing liquid by channeling through the lower part of the tower.

5. *Gas-liquid equilibrium relations.* Turning to the matter of SO₃ equilibrium, one can find the partial pressure over the effluent acid from Fig. 6-8. At 122°F (50°C) the pressure of pure SO₃ is 1000 mm. At the weight fraction of 0.26 for SO₃, the Henry's-law constant is 0.070.* The product of these three quantities, 18.2 mm, is the partial pressure of SO₃ over the liquid. This contrasts with the partial pressure in the gas,

$$0.099(820) = 81.2 \text{ mm}$$

which is more than four times the back pressure over the liquid. This in turn should result in rapid SO₃ absorption at the tower bottom. This is another factor that should raise bottom-liquid temperature. At the top of the tower the liquid temperature is 53.3°C, which corresponds to a vapor pressure of 1185 mm for pure SO₃. At a weight fraction of SO₃ of 0.23, the Henry's-law coefficient corrected for temperature is 0.065, whence the partial pressure of SO₃ over the liquid is 17.7 mm. This is in

* The numerical value of the Henry's-law constant, which expresses the proportionality between the vapor pressure of a solute and its concentration, depends upon the units chosen for pressure and concentration. In this case, 0.070 is the value of P/P_{ow} as read from Fig. 6-8 for the conditions of the problem. While it is proportional to the ratio of P to concentration, it is not the Henry's-law constant of the physical chemist, which is $k = P/x$, where x is mol fraction.

contrast to that in the gas, $0.017(810) = 13.8$ mm. Presumably a little desorption occurs in the very top of the tower.

6. *Possibility of making 30 per cent oleum.* If bottom-liquid concentration is to rise to 30%, the Henry's-law coefficient becomes 0.085, which raises the back pressure of SO_3 over it to 25.5 mm. However, the SO_3 in the entering gas is still over three times as great as this, so the driving force at this point is ample.

Illustration 9. A contact sulfuric acid plant, which has been making 98% acid as its only product, has the problem of increasing its capacity by producing an additional 1800 lb/hr of oleum containing 20% free SO_3 . This is to be done in a new unit. The gas going to the absorption system of the new unit will contain 12% SO_3 . It is proposed to have two absorbers in series, both provided with recirculation lines to take acid issuing from the bottom of each tower and recirculate it through a cooler to the top of the tower from which it came. These coolers will be designed to maintain the acid leaving them at 25°C. Coolers will be provided on the gas line bringing in the converted gas and also on the line carrying the gas from the first absorber to the second, both lines designed to bring these gases to 25°C. There will be no internal cooling in either of the towers. The second gas cleanup absorber is to have 98% H_2SO_4 entering its top from the cooler.¹ It is also agreed to build up the concentration of the acid flowing down the second tower to 102% H_2SO_4 and adjust that of the acid fed to the top of the first tower to 10% oleum. The total water requirement of the system for the chemical formation of the acid is to be supplied to the recycle line of the second absorber and will be available at 15°C. The first absorber unit is supplied with the net production of acid from the bottom of the second, and the plant product, 20% oleum, is to be drawn off from the bottom of the first. The product will flow through a cooler of sufficient capacity to reduce its temperature to 25°C.

Sketch the two absorbing units, indicating all essential connections. Estimate the flow rates in all streams in the system and the heat abstracted hourly in each of the coolers, these data to serve as the basis of detailed design of the construction and operation of the coolers and towers.

Solution. Figure 6-10 is a diagrammatic sketch of the operation as agreed upon in the statement of the problem, with the original numerical data entered on it.

There are four streams of liquid acid in the operation, all of which have different compositions. These compositions are given as weight per cent and are obviously not directly comparable. Because the sulfuric acid,

¹ Industrial experience has demonstrated that a deviation of as little as 1 or 2 per cent from this concentration, in either direction, creates serious mist nuisance in the surrounding atmosphere. The exact optimum concentration is somewhat uncertain.

which constitutes 80% of the product, is formed by chemical combination of sulfur trioxide and water, it seems preferable to express the compositions of these streams on a molal basis. This has been done in the follow-

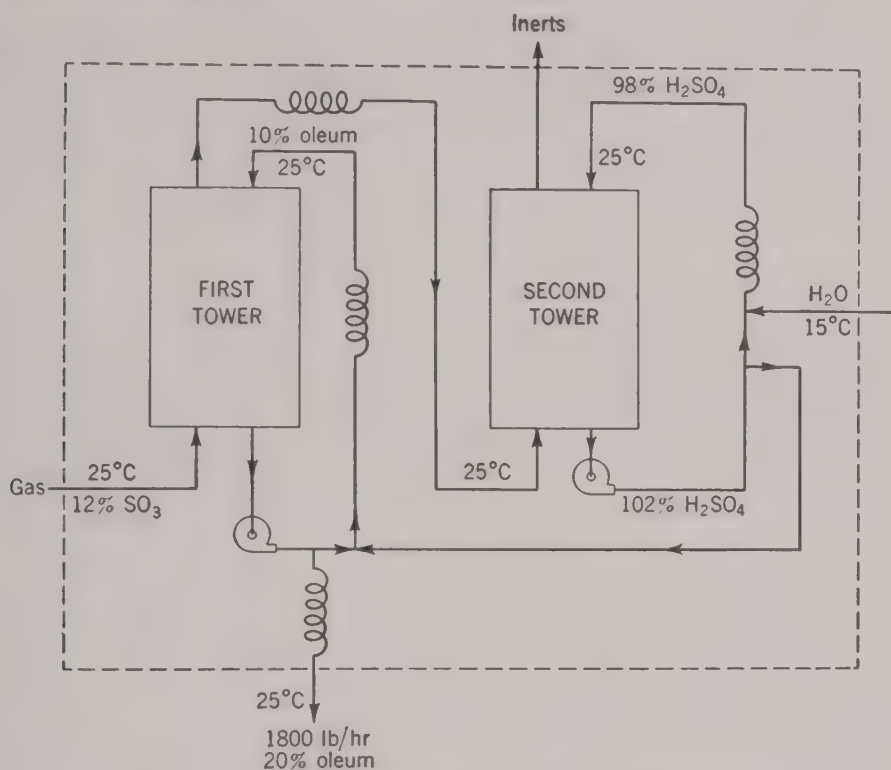


FIG. 6-10. Illustration 9. Original data.

ing table, which gives the mols of each constituent present in 100 lb of each stream. These results will be used repeatedly in the further solution of the problem.

Basis	Mols free H_2O	Mols free SO_3	Mols H_2SO_4	Mols total SO_3
100 lb 20% oleum.....	0.250	0.817	1.067
100 lb 10% oleum.....	0.125	0.919	1.044
100 lb 98% H_2SO_4	0.111	1.000	1.000
100 lb 102% H_2SO_4	0.111	0.930	1.041

In problems of this type, involving recycle streams, those streams whose flow rates are known are usually the external rather than the internal ones. In such a case, it is always advisable initially to take an over-all view of the plant, ignoring the recirculation and focusing on the balances for the operation as a whole, *i.e.*, the streams crossing the dotted lines of Fig. 6-10.

Basis: 1 hr.

	<i>Mols</i>
Total SO ₃ in product, 1.067(1800/100).....	19.20
H ₂ SO ₄ in product = H ₂ O added, 0.817(1800/100).....	14.71

The amount of SO₃ leaving the second absorbing tower in the waste top gas has to be kept negligible, not so much because of its value as to avoid the nuisance of escaping fumes. In consequence, the SO₃ gas entering the plant at the bottom of the first tower is also 19.20 mols. The inert gases entering with it are, in view of the gas analysis,

$$19.2(88/12) = 140.8 \text{ mols}$$

These inerts leave the system from the top of the second tower.

This knowledge of the amount of each component in the various streams entering and leaving the plant determines the over-all heat effect, *i.e.*, the change in enthalpy. The thermal data used in the following calculations are taken from Figs. 6-1 and 6-6. It should be noted that in Fig. 6-6 the enthalpies plotted are always per pound of the mixture in question.

Basis: 1 hr. Base temperature, 64°F.

	<i>Btu</i>
Enthalpy of entering streams:	
SO ₃ in gas stream at 25°C (77°F), 19.20(11.9)(77 - 64).....	2,970
H ₂ O at 15°C (59°F), 14.71(18)(59 - 64).....	-1,324
Total.....	1,646
Enthalpy of product:	
20% oleum at 25°C, 1800 (-525).....	-945,000
Total heat evolved, 1646 - (-945,000).....	946,600

Thus, no matter what happens inside the plant, if both the oleum product and the waste gases are brought to 25°C, the total heat that must be removed by the coolers in the system is 946,600 Btu/hr.

These results are shown in Fig. 6-11.

The above completes the information obtainable from over-all balances. One must now study what is happening within the system.

The amount of SO₃ absorbed in each tower and the corresponding recycle can be determined from total SO₃ and H₂O balances on each tower, *i.e.*, from the changes in composition in the acid streams between the top and bottom of the towers and from the amount of water added. Start by considering the second or cleanup tower. Just as it was best to start with over-all balances on the whole plant, so here it is best to start with over-all balances on the single tower. Thus, mere inspection of Fig. 6-11 shows that all the 14.71 mols of water entering the recycle line of the second tower leaves in the 102% acid stream flowing from the second tower to the

first, although present in that stream as H_2SO_4 . Hence, by a water balance, the amount of total SO_3 in this acid stream is

$$14.71(1.041/0.930) = 16.48 \text{ mols } \text{SO}_3 \text{ per hour}$$

A corresponding SO_3 balance shows that this same quantity, 16.48 mols, is both the total SO_3 absorbed per hour in the tower and the SO_3 in the gas

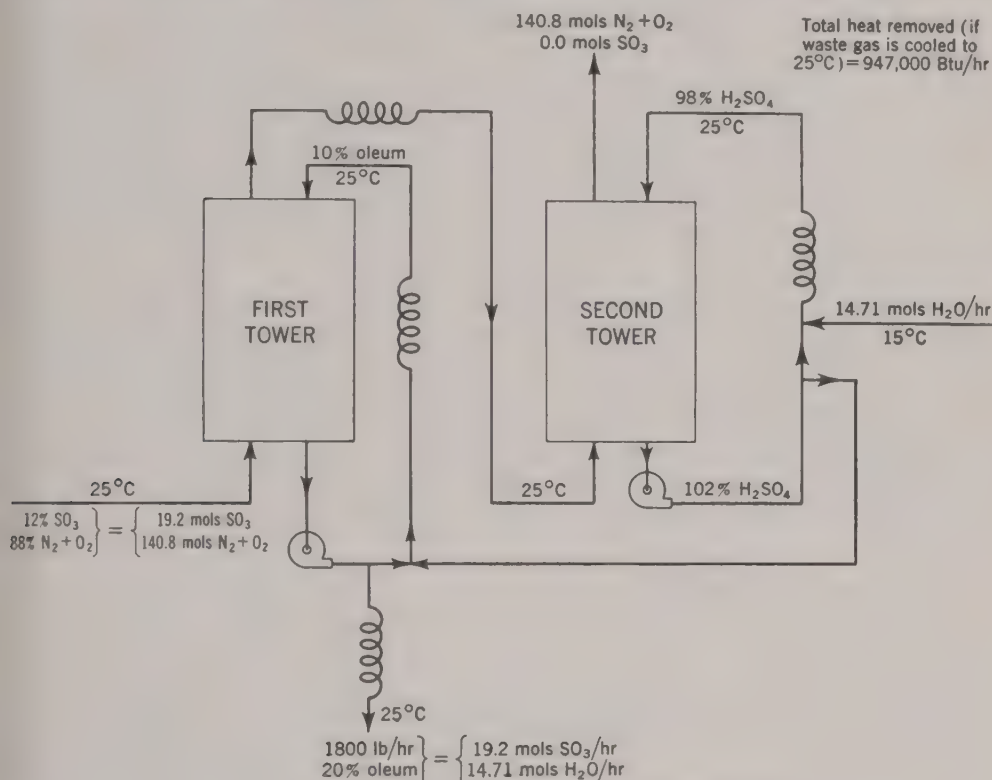


FIG. 6-11. Illustration 9. Results of over-all balances.

flowing hourly from the first tower to the second. In view of the compositions, the hourly flow rates of the two streams are

$$16.48(100/1.041) = 1584 \text{ lb}$$

for the acid and $16.48 + 140.8 = 157.28$ total mols of gas. The mol fraction of SO_3 in the entering gas is $16.48/157.3 = 0.1047$, which, since the pressure is atmospheric, is also the partial pressure of the SO_3 in this gas, expressed in atmospheres.

Referring again to that portion of Fig. 6-11 relating to the second tower, one sees that three flow rates are still unknown, *i.e.*, the acid stream entering the top, that leaving the bottom, and that recycled to the point of water injection. Because the SO_3 absorbed in the tower is known (16.48 mols), together with top and bottom acid compositions, the amount of the

downflowing acid stream can be calculated by an SO_3 balance. Because the total water entering the top equals that leaving the bottom, this balance is conveniently set up on a water basis.

The molal ratio of total SO_3 to H_2O in the 98% acid entering the top of the tower is $1.000/(1.000 + 0.111) = 0.900$. The corresponding ratio in the 102% acid leaving is $1.041/0.930 = 1.120$. Thus, to absorb 16.48 mols of SO_3 , there must be $16.48/(1.120 - 0.900) = 74.9$ mols of total water entering in the 98% acid and leaving in the 102% acid. This corresponds to $74.9(100)/(1.000 + 0.111) = 6725$ lb of 98% acid entering the top of the tower and $6725 + (16.48)80 = 8044$ lb of 102% acid leaving the bottom. Of this latter, 1584 lb of 102% acid is sent to the first tower and the remainder, 6460 lb, is recycled. To this 6460 lb of recycled 102% acid are added 14.71 mols (265 lb) of water, giving 6725 lb of 98% acid to the top of the tower.

The same type of reasoning may be applied to the first tower. Since 19.2 mols/hr of SO_3 enter the first tower and 16.48 leave, the absorption of SO_3 is 2.72 mols/hr. Each hour, 14.71 mols of H_2O (present as H_2SO_4) enter in the 102% acid and leave in the 1800 lb of oleum. The molal ratio of total SO_3 to H_2SO_4 in the 10% oleum entering the top of the tower is $1.044/0.919 = 1.138$, and in the 20% oleum leaving the bottom it is $1.067/0.817 = 1.307$. To absorb 2.72 mols of SO_3 requires

$$2.72/(1.307 - 1.138) = 16.11 \text{ mols of } \text{H}_2\text{SO}_4$$

in the 10% oleum entering and in the 20% oleum leaving. This corresponds to $16.11(100/0.919) = 1755$ lb of 10% oleum entering the tower and $1642 + 2.72(80) = 1973$ lb leaving the bottom. The recycle will be this 1973 lb minus the 1800 lb drawn off as product, *i.e.*, 173 lb/hr.

The heat effects in the system can be determined by enthalpy balances. Thus, Fig. 6-6 shows that the enthalpy above 64°F per pound of 98% acid entering the top of the second tower at 25°C is -576 Btu. Similarly, the enthalpy per pound of 102% bottom acid is -554 Btu. Because Fig. 6-6 is constructed on the assumption that the gaseous SO_3 on which it is based is at 64°F, a correction is necessary at this point for the enthalpy of the SO_3 which enters the tower at 25°C (77°F), or 13°F above the 64°F base of the chart. No correction for the inerts is necessary at this point because they neither contribute to the heat evolution nor enter in any way into the construction of Fig. 6-6. The SO_3 correction can be obtained from the heat capacity given by Fig. 6-7, namely,

$$16.48(11.9)(77 - 64) = 2550 \text{ Btu/hr}$$

Therefore, the change in enthalpy in the tower is

$$6725(-576) + 2550 - 8044(-554) = 573,000 \text{ Btu/hr}$$

This figure is the hourly heat evolution in the second tower. However, this does not answer the question as to where the heat goes. Since there are no cooling coils in the tower itself, if one neglects heat losses through the walls, this heat must be taken out of the tower in the two streams leaving it, namely, the top waste gas and the bottom acid. The problem of the distribution of heat between two streams has been discussed in Chap. 3 for conditions of heat exchange but not for a case entirely analogous to this one.

The heat evolved in the second tower is the heat of absorption of the gaseous SO_3 in the liquid stream. This absorption occurs throughout the tower, but for the purpose of discussion, assume for the moment that all the absorption and therefore all the corresponding heat evolution occurs in a relatively narrow zone somewhere in the middle of the tower. This zone will be at a high temperature level, and both the downward-flowing liquid and the upward-flowing gas leaving it will be hot. Each, however, flows from the absorption zone to its point of outlet from the tower in contact with a cold stream of fluid with which it is in counter-current heat exchange. The discussion of Chap. 3 makes it clear that in such a countercurrent-heat-exchange operation the stream of lower heat capacity tends to leave the exchanger in thermal equilibrium with the entering stream of higher heat capacity, and in the limiting case equalization of temperature of the two streams at that point will result. Therefore, to visualize what is happening within the tower it is imperative to know the heat capacities of its streams.

	Btu/(hr)(°F)
Heat capacity of the 98% acid entering the tower, 6725(0.340).....	2280
Heat capacity of the 102% acid leaving the tower, 8044(0.325).....	2610
Heat capacity of the gas entering the tower:	
SO_3 , 16.48(11.9).....	196
Inerts, 140.8(7.0).....	985
	1181
Heat capacity of the gas leaving the tower 140.8(7.0)	985

As the acid flows down, absorbing SO_3 , its heat capacity increases, while the heat capacity of the gas flowing up the tower decreases, as it loses SO_3 , to a final value of 985 Btu/hr/°F at the top. It is seen that the heat capacity of the feed stream of acid entering the second tower is more than twice as large as the heat capacity of the gas stream leaving that tower; at the tower bottom the ratio of the heat capacities of the liquid and gaseous streams is still above 2. Consequently, in so far as the top and bottom of the tower act as countercurrent heat exchangers, the bottom stream of acid will tend to go out hot and the top stream of gas will tend to go out cold. This is equivalent to saying that all the sensible heat in the gas stream as it leaves the absorption section of the unit postulated above

tends to be transferred to the acid stream and carried back into the absorption section. Similarly, the gas stream flowing upward through the bottom part of the tower will be heated by the acid stream flowing counter to it and will tend to enter the absorption section at the temperature of the acid leaving it, which in turn would presumably be substantially identical to the temperature of the absorption zone itself. In other words, the effect is to feed sensible heat into the absorption zone in both the acid and gas streams entering it, in addition to the heat of absorption released in the zone itself. This results in a corresponding rise in temperature in the absorption zone. The tower tends to get very hot in the middle, but the heat tends to come out of the tower as a whole in the form of sensible heat in the bottom acid leaving it.

As already indicated, what really happens is not segregation of SO_3 absorption into a narrow zone in the middle of the tower. Absorption and heat exchange by counterflow are occurring simultaneously throughout the whole tower, but the tendency described above still remains. This is particularly true at the top of the tower, where, for satisfactory operation, SO_3 concentration is necessarily very low and absorption correspondingly negligible. Hence, the top of the tower functions, as described above, predominantly as a heat exchanger, without significant complications due to concomitant absorption. In so far as this is true, it is equivalent to saying that the conditions at the top of the tower are very effective in forcing all the heat evolved in the tower to leave in the bottom-acid stream. This also results in concentrating most of the absorption and hence most of the heat evolution in the lower part of the tower. Because the performance of a counterflow heat-exchange operation such as exists at the top of the tower will not bring complete equilibrium of entering and leaving streams, some heat will in fact leave in the form of sensible heat in the top waste gas, lowering the temperature of the bottom acid correspondingly. The determination of the actual course of the absorption and of the distribution of the heat in the tower is a design problem in absorption, which is outside the scope of this text. On the other hand, the material and enthalpy balances, together with a qualitative picture of what is going on in the tower, enable one to calculate the maximum temperature attainable by the bottom-acid stream and to realize that this limiting condition will be at least approximated in the actual performance of the tower.

While there is no significant uncertainty as to the limiting conditions of both acid and gas at the top of the tower, at the bottom there is some uncertainty, because the entering gas and leaving liquid need not be and will not be in thermal equilibrium and, in general, will not be in SO_3 vapor-pressure equilibrium either. In order for the tower to function, the partial pressure of SO_3 in the gas entering the bottom must be in excess of

the back pressure of SO_3 over the acid leaving the tower at that point. By the methods outlined here it is possible to determine, for the limiting conditions, if an excess SO_3 pressure is available.

The 8044 lb/hr of 102% acid at the bottom of the tower carries out 573,000 Btu/hr. The specific heat of the acid is 0.325 (Fig. 6-7). The temperature of the acid above the base of 25°C (77°F) is

$$573,000/8044(0.325) = 201 \text{ Fahrenheit degrees}$$

giving an exit temperature of 288°F (143°C).

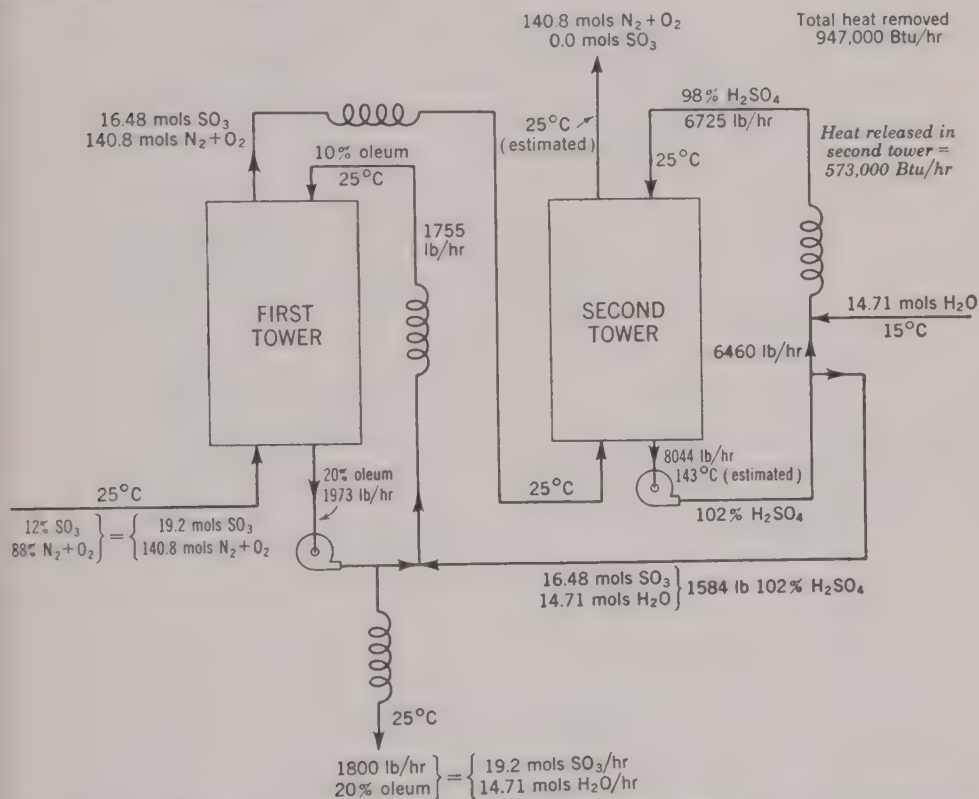


FIG. 6-12. Illustration 9. Results of balances around each tower. The conditions at the bottom of the second tower are such as to make it inoperable.

The results of all calculations up to this point are summarized by the flow sheet of Fig. 6-12. The critical point, as noted above, is the bottom of the second tower. While Fig. 6-8 is not applicable to such a high temperature, it is obvious from it that the vapor pressure of SO_3 in the 102% H_2SO_4 leaving the bottom of the tower at 143°C is greater than 0.1047 atm, the partial pressure of SO_3 in the entering gas. In short, the tower is inoperable under the conditions assumed.

If the H_2SO_4 can be drawn off at a lower temperature, the process can be made to operate but heat has to be removed from the tower itself.

Cooling coils could be installed in the lower part of the tower, but they would complicate operation and maintenance. The 102% H_2SO_4 can be used as a cooling medium by introducing cooled recycle acid into the middle of the tower, as shown in Fig. 6-13. Although this requires a separate cooler, it keeps the bottom-acid concentration unchanged.

It is desirable to estimate the amount of such recycle acid required to make the tower function satisfactorily, *i.e.*, to keep the back pressure

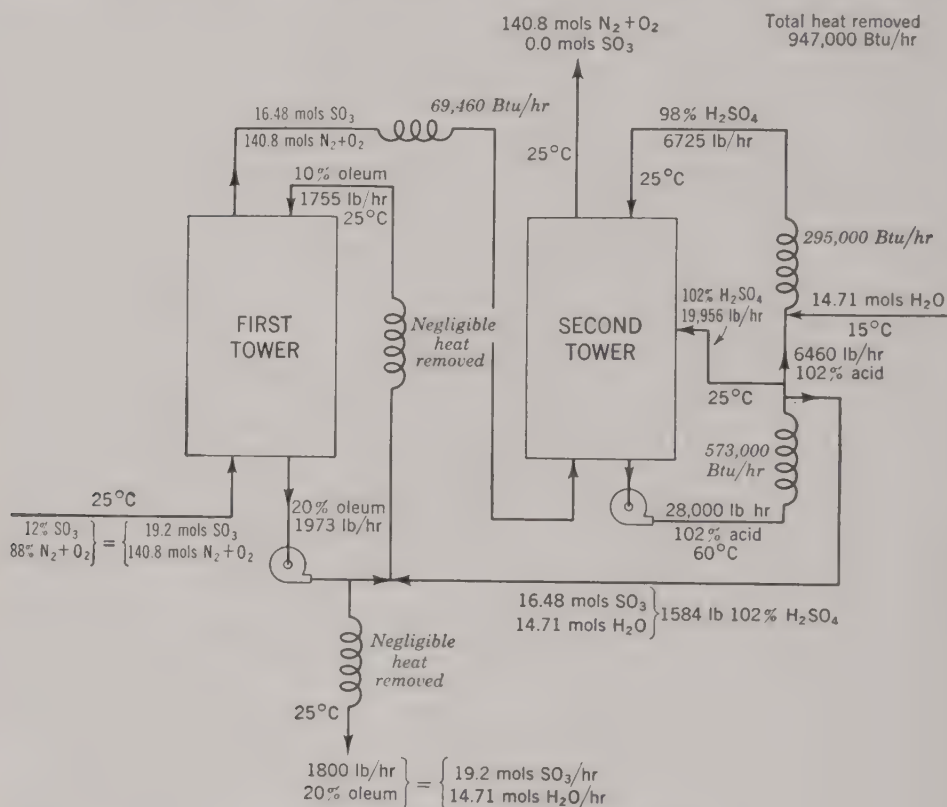


FIG. 6-13. Illustration 9. Final flow sheet.

of SO_3 over the bottom acid adequately below the partial pressure of the SO_3 in the gas entering the bottom of the tower, 0.1047 atm. In the limiting case this would be the SO_3 back pressure of the acid.

In the terminology of Fig. 6-8, this is the quantity P in the ordinate of the plot. Since the concentration w of the acid is known, evaluation of the ordinate determines the pressure P_0 of pure SO_3 at the temperature of the bottom acid, and P_0 in turn determines the temperature of that acid.

As it happens, 102% acid, containing as it does only 8.89% by weight of SO_3 , is on the very flat part of the curve of Fig. 6-8. In other words, it is in a range of concentration in which considerable variation in tempera-

ture has a negligible influence on the value of the ordinate, 0.06. Hence,

$$P_0 = 0.06 w/P = 19.66 \text{ atm} = 14,930 \text{ mm Hg}$$

This is outside the range of Fig. 6-8, although extrapolation would indicate a temperature of roughly 125°C. In any event, one should operate with a factor of safety that will ensure beyond all peradventure an adequate partial-pressure driving force at the bottom. For the moment, assume a bottom-acid temperature of 60°C. Figure 6-8 shows that the SO₃ back pressure over it is 8.6 mm Hg. Because, granting cold top gas, this bottom acid still brings out of the tower all the heat liberated in it, the quantity of the acid is $573,000 / (0.325)(60 - 25)(1.8) = 28,000$ lb/hr. Since the net bottom acid is 8044 lb hourly, the 102% acid recycled to the tower itself is 19,956 lb. This recycle ratio of somewhat over 2:1 gives a large factor of safety in tower bottom temperature and SO₃ back pressure.

Straightforward enthalpy balances show that the heat effect of absorption in the first tower is 69,460 Btu/hr, while that of mixing the 102% acid with the recycle oleum is negligible. The component balances together with the heat-capacity data show that in this tower the total heat capacity of the gas stream is nearly double that of the liquid. This means that the heat evolved in the tower will leave predominantly in the gas flowing from it to the second unit. In consequence, it may well prove to be unnecessary to use liquid coolers for the first tower. The heat load on the gas cooler between the first and second towers is this 69,460 Btu/hr. That on the 98% acid cooler for the second tower can be computed by enthalpy balances; the result is entered on Fig. 6-13.

Illustration 10. The calculations of the preceding problem show that the operation there described is highly unbalanced in that a large fraction of the absorption occurs in the second tower and an even larger fraction of the heat generated is released in that tower. As a matter of good engineering, it is obviously desirable to have a more nearly balanced absorption and heat load between the two towers. Thus, if the two towers perform substantially the same function, a single standby tower can be used to replace either of the two main towers in case of necessity for shutdown of one of them for repairs. A simplified flow sheet with no recycle stream to the middle of either tower and a single recycle cooler for each tower would make for easier control of the unit. Study of the situation makes it clear that, while balance can be greatly improved by a variety of changes, complete equality in both absorption and heat evolution is evidently impossible to achieve. To illustrate the method of approach to the solution of a problem of this sort, the flow sheet of a two-tower unit in which the gas and acid streams entering each tower are cooled to 25°C, with liquid recycle in each tower, will be developed to give approximately equal heat absorption in the two recycle coolers.

Solution. In approaching the solution of this problem, full advantage should be taken of the experience gained in solving the preceding one. This experience can be valuable despite the fact that the layout there developed was thoroughly unsatisfactory. The following generalizations based on Illustrations 8 and 9 are important in any effort to improve the situation.

First of all, as noted in Illustration 9, the concentration of the acid fed to the top of the second tower is fixed by the necessity of preventing mist formation and should be maintained at approximately 98%.

In the second place, the energy balances of Illustrations 8 and 9 show that the heat evolved per mol of SO_3 absorbed is higher in a cleanup tower than it is in an oleum tower. For example, if SO_3 vapor at 64°F is added to 98% acid at 64°F to produce 100% acid at 64°F , the data of Fig. 6-6 show that the heat evolved is 570 Btu per pound of SO_3 absorbed. If SO_3 vapor at 64°F is added to 15% oleum at 64°F , the corresponding figure is only 320 Btu per pound of SO_3 absorbed. Therefore, it is impossible to make the amount of SO_3 absorbed in one tower equal to that in the other if the heat evolved in the two towers is the same.

How important is it to equalize the evolution of heat in the first tower with that in the second? The answer to this question depends on whether or not the heat evolved within the towers is an important fraction of the heat removed in the recycle coolers. Taking a rough average figure of 450 Btu evolved per pound of SO_3 absorbed, it is found that the evolution of heat within the towers is approximately

$$450(19.2)(80) = 690,000 \text{ Btu/hr}$$

or almost three-quarters of the total heat to be removed from the unit (947,000 Btu/hr). Therefore, if the evolution of heat within the two towers can be equalized, this will be a long step toward balancing the load on the coolers. To secure a balance, the mols of SO_3 absorbed in the first tower should be to the mols absorbed in the second tower as 570 is to 320.

The other point in the unit at which significant evolution of heat occurs is the point at which water is introduced. If this heat is to be distributed more evenly between the two recycle coolers, part of the water must be sent to the first tower and part to the second. However, the distribution of water between the two towers is affected by concentrations at various points within the unit, and these in turn are affected by the amounts of recycle employed. In order to keep the diameter of each tower at a minimum, one would like if possible to use the smallest amount of recycle consistent with the allowable rise in temperature of the bottom liquid, discussed under Illustration 8. A logical approach, then, is to assume the amounts of recycle on this basis and see if the corresponding

distribution of water in the system gives a reasonably balanced distribution of heat load between the two coolers.

In the light of Illustrations 8 and 9, the recycle to each tower should have enough heat capacity to absorb the heat evolved in the tower without an excessive rise in the temperature of the bottom liquid. The minimum amount needed in each case can be readily estimated from a consideration of the heats of absorption, the allowable temperature rise, and specific heats.

On the basis of the discussion of vapor-liquid equilibrium in Illustrations 8 and 9, the 345,000 Btu/hr evolved in each tower must be absorbed without causing the temperature to rise above about 60°C. Figure 6-7 indicates that the specific heats of the liquids in the two towers are about the same and approximately equal to 0.34. Therefore, the minimum allowable recycle in each case is $(345,000)/(60 - 25)(1.8)(0.34)$, or 16,000 lb/hr.

In view of the discussion of heat capacities in Illustration 9 and the large ratio of liquid to gas in each tower in the present case, the top gas from each tower must leave at a temperature quite close to 25°C.

These generalizations, obtained from the work of Illustrations 8 and 9, suggest the nature of the simplifying assumptions to be made in the first attempt to lay out a flow sheet. As a first approximation, assume the following:

1. The concentration of the acid entering the top of the second tower is 98%.
2. In the first tower 12.3 mols of SO_3 per hour are absorbed and in the second 6.9 mols/hr.
3. The rate of flow of liquid from the bottom of each tower is 16,000 lb/hr.
4. The top gas from each tower is at 25°C.

These assumptions, together with the original statement of the problem, are sufficient to fix the flow rates and compositions of all streams in the system and the heat duty on each of the recycle coolers. The calculations, exactly the same in principle as those of Illustration 8, lead to the results entered on the flow sheet in Fig. 6-14.

Inspection of Fig. 6-14 reveals that the heat load on the recycle cooler of the first tower is about 40% higher than that on the cooler of the second tower. Evidently, too much water is being sent to the first tower, and an adjustment of some kind is necessary.

One possibility is to increase the amount of recycle to the second tower. This step would decrease the concentration of the acid flowing from the second tower to the first and thereby increase the amount of water fed to the second tower. However, the concentration of this acid is already close to its limiting value of 98%, and little improvement can possibly

be achieved by a further change in this direction. A more promising alternative is to make a slight increase in the amount of SO_3 absorbed in the second tower. While this will mean that the heat evolved within the second tower will be greater than that within the first, the change will not be great and the fact that the first trial indicated a temperature of only 54°C at the bottom of the second tower shows that some increase

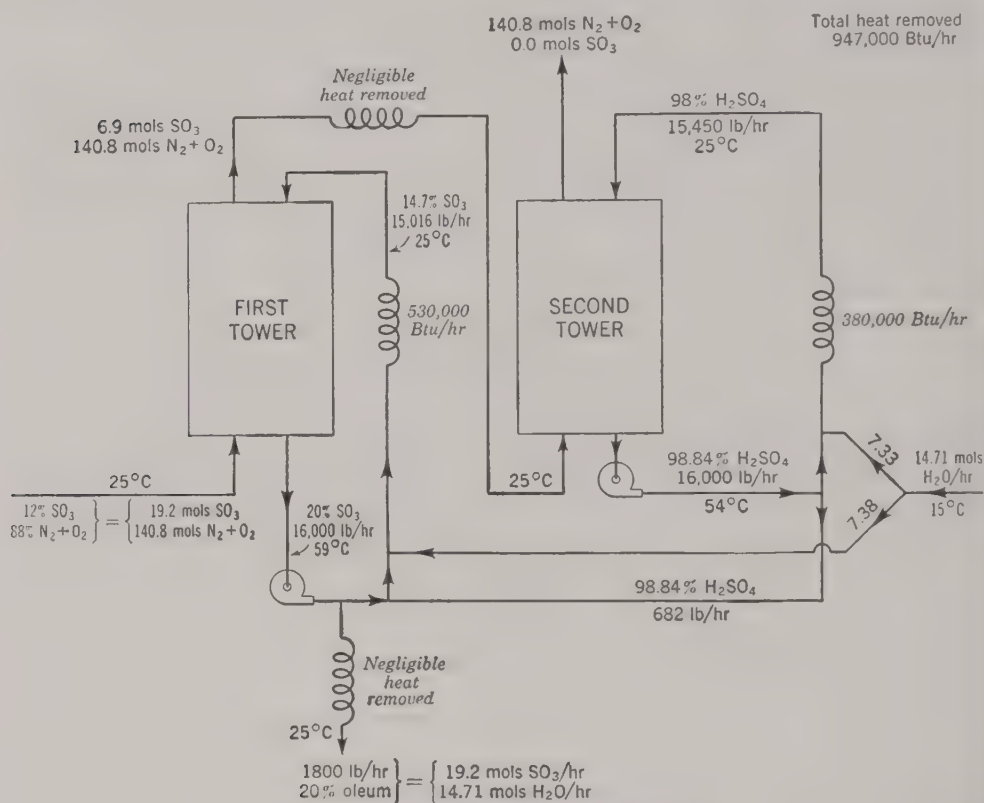


FIG. 6-14. Illustration 10. First trial.

in the temperature at that point can be tolerated. Furthermore, adjustment of the SO_3 absorbed will bring both the absorption loads and the heat duties on the coolers more nearly into balance.

Figure 6-15 represents the results of calculations in which the same assumptions were made as before, except that the mols of SO_3 absorbed per hour in the first and second towers were taken to be 10.8 and 8.4, respectively. In the flow sheet of Fig. 6-15 the heat loads on the two recycle coolers are practically equal, and the amounts absorbed in each tower are not far from equal. However, the liquid at the bottom of each tower is not quite so close to equilibrium with the entering gas as it might be. In the first tower the temperature of the bottom liquid is only 52°C , whereas the calculations of Illustration 8 indicated that 60°C would

not be at all excessive. In the second tower the temperature of the bottom liquid is slightly above 60°C, but one should recall that the limit of 60°C at this point was originally chosen on the basis of Illustration 9, in which the concentration of the bottom liquid was 102% H₂SO₄. In the present flow sheet the concentration of the bottom liquid is only 99% H₂SO₄, over which the partial pressure of SO₃ is extremely low.

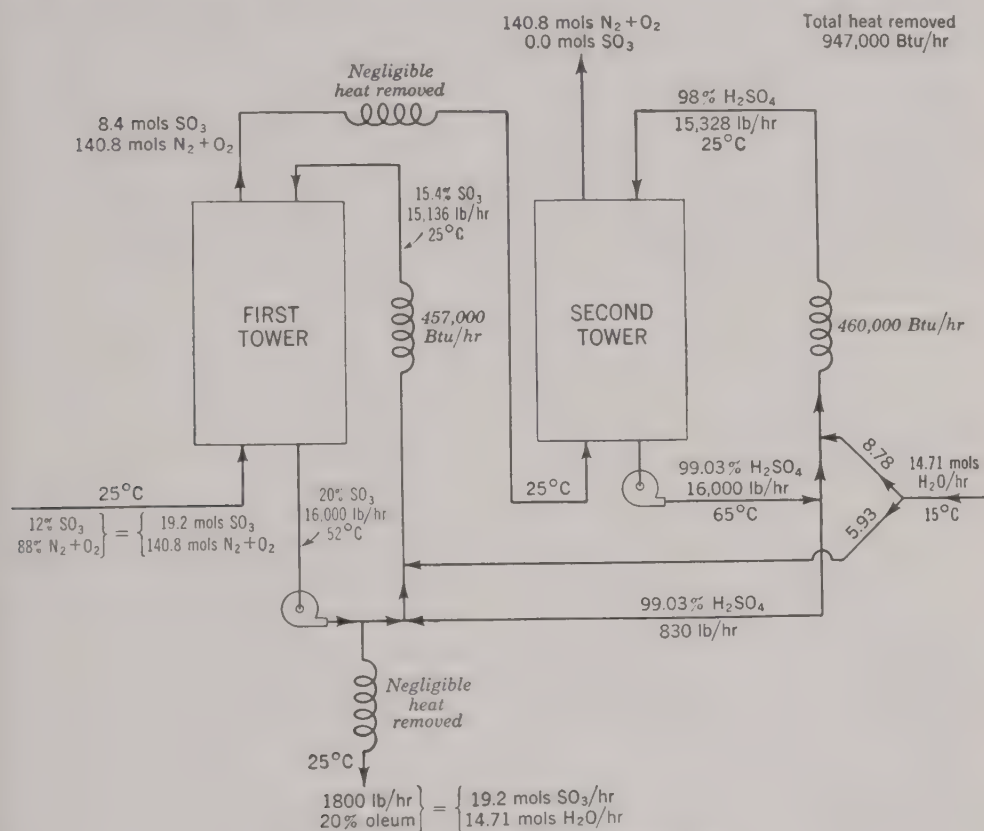


FIG. 6-15. Illustration 10. Second trial.

The way to take advantage of the situation is to reduce slightly the rate of recycle to each tower, which will tend to reduce the size of towers, pumps, and lines required. As mentioned previously, a reduction in the recycle will affect the concentrations at various points within the system and also the distribution of water between the two towers, with the net result of increasing the heat load on the recycle cooler of the first tower and decreasing the load on the recycle cooler of the second tower. To keep the heat loads in balance there should be a slight shift of SO_3 absorption from the first tower to the second as the recycle to the towers is reduced. The extent to which the recycle can be reduced and the absorption shifted without upsetting the balance of the heat relationships or causing an excessively high partial pressure of SO_3 over the

bottom liquid of either tower requires the development of further trial flow sheets. Clearly, the final arrangement will not differ greatly from Fig. 6-15.

Note that the key to the problem is successive approximation.

PROBLEMS

1. A contact sulfuric acid plant, operating smoothly and efficiently, burns sulfur of high purity in a conventional rotary burner with a brick-lined steel shell. The burner gases flow through a jet injector into a secondary combustion chamber of brick enclosed in thin welded sheet steel and thence to the coolers. Three gas samples are withdrawn from the system: the first from the gases leaving the rotary burner and flowing to the injector, the second from the gases flowing from the injector to the secondary combustion chamber, and the third from the gases entering the coolers. The techniques of sampling and analysis have been tested and found to be dependable, and the analyses tabulated below are representative of normal operation of the plant.

Gas	Per cent		
	Sample 1	Sample 2	Sample 3
SO ₂	11.75	8.63	9.66
O ₂	8.89	12.00	10.87
N ₂	79.36	79.37	79.47

(a) What per cent of the total amount of O₂ reacting in the system reacts in the secondary combustion chamber?

(b) Calculate the percentage of the total sulfur charged to the burner that enters the secondary combustion chamber in the form of sulfur vapor.

(c) What per cent of the total air supplied to the system enters the rotary burner as primary air?

2. A contact sulfuric acid plant is burning sulfur in a rotary burner the gases from which pass into a secondary combustion chamber constructed with double refractory walls. The secondary air enters through the space between these walls, flowing counter to the combustion gases, and is introduced in the conventional way into the stream of burning gases at the point at which they pass from the rotary burner into the secondary combustion chamber. The following data are available on the performance of this unit: The final burner gases going to the catalyst unit contain 7.88% SO₂, 12.68% O₂, and 79.44% N₂. The preheated air just before entering the burner-gas stream is at 562°C and contains 2.62% SO₂, 17.96% O₂, and 79.42% N₂. A sample of the burner gases taken just prior to mixing with the secondary air is collected through a water-cooled tube and shows 15.06% SO₂, 5.46% O₂, and 79.48% N₂. All these analyses are carefully made by conventional techniques, with mercury as the confining fluid. Another sample duplicating the last of these as to time and point of collection is analyzed as follows. The sample as it is being withdrawn is mixed without drop in temperature with a stream of pure oxygen gas, and the mixture is drawn slowly through a silica tube at 900°C before being cooled for analysis. The cooled sample is drawn through a well-designed bubbler bottle containing 100 ml of N/50 NaOH, and the undissolved gas is collected and measured. The residual volume of

gas, reduced to dry standard conditions, amounts to 95.5 ml. Analysis shows it to contain 9.14% O_2 and 90.86% N_2 . The excess NaOH in the bubbler is titrated with $N/50$ HCl, with phenolphthalein as indicator, and consumes 15.5 ml. Construct a flow sheet of this unit and indicate on it the following quantities, computed on a basis of 100 atoms of sulfur burnt:

(a) Mols of SO_2 and mols of SO_3 in the gases leaving the secondary combustion chamber.

(b) Mols of SO_2 , mols of SO_3 , and atoms of S present as sulfur vapor in the gases leaving the burner, prior to admixture of secondary air.

(c) Mols of primary air supplied to the burner and mols of secondary air entering the space between the walls of the secondary combustion chamber.

(d) Mols of gas leakage from the secondary combustion chamber to the space between its walls. Assume that the gas leakage has the same composition as the gases leaving the secondary combustion chamber. What is your opinion of the reasonableness of this assumption?

3. The rotary burner and the outside wall of the secondary combustion chamber of Prob. 2 are well lagged, and heat losses to the surroundings are small. The sulfur is melted by heat conducted to the feed hopper from the burner.

(a) Compute the temperature in degrees centigrade of the gases leaving the secondary combustion chamber and flowing to the converter system.

(b) On the assumption that the temperature of the gas leaking from the secondary combustion chamber into the space between its walls is the same as that of the gases flowing from the secondary combustion chamber to the converter system, estimate the heat flow by conduction through the inner wall of the secondary combustion chamber. Express the result in Btu per 100 atoms of sulfur burnt.

4. In each of the following cases, what do the facts given mean to you?

(a) A pyrites burner using an FeS_2 ore of high purity gives a burner gas the analysis of which by conventional technique over mercury shows an average over a 24-hr test period of 8.64% SO_2 and 11.40% O_2 .

(b) A pyrites burner using an ore containing 45.70% S, 44.25% Fe, and only small amounts of other sulfide-forming heavy metals gives a gas the average composition of which is 9.07% SO_2 and 5.39% O_2 as determined by conventional analysis over mercury.

5. A pyrites burner is roasting an ore that analyzes 45.2% Fe and 50.4% S on a dry basis. The cinder contains 60.8% Fe and 5.9% S, and the composition of the gas is 8.90% SO_2 , 7.98% O_2 , and 83.12% N_2 , as determined by conventional technique.

(a) How many mols of dry air are used by the burner per 100 lb of ore fired?

(b) The unit is of the countercurrent type, similar to a Herreshoff burner. The inerts in the ore have a heat capacity of $0.17 \text{ Btu}/(\text{lb})(^\circ\text{F})$, and the sulfur in the cinder may be presumed to be present as adsorbed SO_3 . If the unit be operated with the same air-ore ratio as at present, but conditions be modified in such a way as to drive the SO_3 from the cinder into the gas and oxidize the cinder completely to Fe_2O_3 , what would be the highest possible temperature of the off gases?

6. A sulfite-pulp mill manufactures its cooking liquor by passing the gases from a sulfur burner in succession through a cooler, an entrainment separator, and then two absorbing towers. The gases, analyzing 18.0% SO_2 , 0.85% SO_3 , 1.10% O_2 , and 80.05% N_2 , pass through the first tower, which is packed with chemical stoneware, countercurrent to weak liquor pumped from the bottom of the second or so-called "weak" tower to the top of the first or "strong" tower. The gases then enter the bottom of the weak tower, which is packed with limestone containing 95.8% $CaCO_3$ and 2.35% $MgCO_3$, where they are scrubbed by a stream of water entering the top of this tower. The vent gases from the weak tower contain 6.19% CO_2 , 0.73% O_2 , and

93.08% N_2 . The water rate to the weak tower is 154,000 lb/hr. The cooking liquor contains 1.04 wt-% combined SO_2 (i.e., SO_2 that cannot be expelled by prolonged boiling) and 5.00 wt-% total SO_2 .

(a) What is the limestone consumption in pounds per hour?

(b) What is the sulfur feed rate to the burner in pounds per hour?

7. A chamber plant burning sulfur produces an acid of 1.71 sp gr and 78.2% H_2SO_4 from its Glover tower. In this particular installation all the chamber acid is sent to the Glover for concentration, and the Glover acid is the entire product. Per pound of plant product, 3.5 lb of acid are circulated from the Gay-Lussac tower to the Glover. This Gay-Lussac acid contains 0.923% N_2O_3 and 77.4% total sulfur as H_2SO_4 . The amount of 100% HNO_3 used is 2.37 lb per 100 lb of sulfur burnt. The waste gas contains 5.8% O_2 . Conversion of sulfur to H_2SO_4 averages 96%. Nitrogen oxides in the gas leaving the last chamber and in the vent gas leaving the Gay-Lussac may be assumed to be present as an equimolal mixture of NO and NO_2 .

(a) Compute the mols of air supplied to the burner per 100 lb of sulfur burnt.

(b) What per cent of the gas leaving the last chamber consists of nitrogen oxides?

(c) By what percentage would a 10% increase in absorption of nitrogen oxides in the Gay-Lussac reduce consumption of nitric acid?

8. Freeman¹ passed three streams of gas continuously into a common tube: first, 18 ml/min of O_2 ; second, 3 ml/min of NO; and third, 279 ml/min of N_2 . The barometer was 766 mm Hg and the atmospheric temperature 24°C. Immediately after the three streams were mixed, the combined stream was bubbled through 20 ml of sulfuric acid solution at 24°C, having a specific gravity of 1.760. At the end of 1 hr a 5-ml liquid sample was removed. Of this, 2 ml in a nitrometer evolved 14.2 ml of gas at 24°C. The rest was introduced into a microburette, whence a measured amount was run into a solution of exactly 2.5 ml of 0.4244 N $KMnO_4$. To discharge the color 1.85 ml of the acid was required. The bubbling was continued for another hour, when the gas evolution was 20.01 ml and the acid consumed in titration 1.31 ml. After a third hour these figures remained practically unchanged. A second run was made with the same O_2 rate, 6 ml/min of NO, and 276 ml/min of N_2 . After 2 hr of bubbling, a 5-ml sample was removed and tested. The nitrometer gas was 28.9 ml, and the acid needed to discharge the $KMnO_4$ was 0.89 ml. Discuss the significance of these figures.

9. In each of the following cases, what conclusions can you draw as to the operation of the converter?

(a) A Pt-on- $MgSO_4$ converter of the conventional, uncooled, fixed-bed type is fed with a gas that has been cooled, scrubbed with sulfuric acid, filtered, and preheated to 400°C. The analysis of the gas as it enters the converter is 10% SO_2 and 10% O_2 . The gas leaves the converter at 550°C, and analysis of it by the usual method with mercury as the confining fluid shows 5.52% SO_2 and 8.15% O_2 .

(b) A Jaeger converter unit has two concentric tubes embedded in the catalyst mass. The inlet gas is preheated by flowing up through the inside tube, then down through the annular space between the two tubes. It then passes into the catalyst mass and flows upward through it, leaving the unit at the top. A converter of this type with V_2O_5 on pumice as the catalyst is fed with the same gas as in part (a). However, in this case the gas enters the unit at a temperature of only 220°C. The gas leaving the unit is at 440°C, and conversion is 96%.

(c) A platinum converter receives gas from a sulfur burner after it is cooled to atmospheric temperature, scrubbed with sulfuric acid, filtered, and reheated to

¹ G. D. Freeman III, research report, School of Chemical Engineering Practice, Massachusetts Institute of Technology, 1934.

400°C. At the entrance to the converter the gas contains 10% SO_2 and 10% O_2 . As it leaves the converter, the temperature of the gas is 504°C, and it contains 4.98% SO_2 and 9.40% O_2 .

10. Because of a special situation, a mining enterprise in British Columbia has comparatively pure sulfur dioxide and oxygen available as raw materials for a contact sulfuric acid plant.¹ The following data are representative of typical operation with the catalyst in good condition: Gas is fed to the converter system at the rate of 6000 cu ft/min (apparently measured at 1 atm and 0°C), and this feed gas has an average composition of 25% SO_2 , 30% O_2 , and 45% N_2 . The SO_3 in the gases leaving the converter system is equivalent to 200 tons of 100% H_2SO_4 per day. The plant operates at substantially atmospheric pressure. The converter system consists of three layers of catalyst with cooling provided after each layer by tubes through which air is circulated. The temperatures at various points are as follows: inlet gas, 402°C; catalyst in first layer, 682°C; gas after first cooler, 586°C; catalyst in second layer, 642°C; gas after second cooler, 557°C; catalyst in third layer, 638°C; outlet gas, 528°C. The air circulating through the first cooler removes 20,780 Btu/min from the system, and the air passing through the second cooler removes 14,980 Btu/min. The heat removed by the third cooler is practically zero.

(a) What is the composition of the gas leaving the converter system?

(b) How much heat in Btu per minute is lost to the surroundings by radiation, etc., from the walls of the converter system?

(c) The construction of the system is such that the total heat losses to the surroundings may be assumed to be divided approximately as follows: one-third of the total is lost between the point at which the temperature of the inlet gas is measured and the point at which the gas leaves the first layer of catalyst; one-sixth, between the point at which the gas leaves the first cooler and the point of exit from the second layer; one-sixth, between the point at which the gas leaves the second cooler and the point of exit from the third layer; one-third, between the point at which the gas leaves the third cooler and the point at which the temperature of the outlet gas is measured; and a negligible amount from the coolers. On the basis of these assumptions estimate the temperature of the gas as it leaves each layer of catalyst.

(d) Estimate by means of energy balances the mols of SO_3 formed in each layer of the catalyst per minute, and calculate the composition of the gas leaving the first layer.

(e) If a gas having the same composition as that computed in part (d) for the gas leaving the first layer of catalyst is at chemical equilibrium, what is its temperature?

(f) This same converter system was formerly used as the converter system in a standard contact sulfuric acid plant, operating in the conventional way with a feed gas containing 8 to 10% SO_2 . Under these conditions the production of SO_3 was equivalent to 35 tons of 100% H_2SO_4 per day. In the light of your calculations, what do you think are the significant differences between the present and former operation of the system? If, instead of using equipment originally designed to handle a conventional feed gas, you were called upon to design a completely new system to handle the present feed gas, in what respect (if any) would your design differ from that of the present setup?

11. The gas from a pyrites burner, containing 8.3% SO_2 , 6.4% O_2 , and 85.3% N_2 , is dried by passing through sulfuric acid, freed from dust in coke filters, and preheated to 400°C before being fed to a platinum converter. The converter is well insulated, and the catalyst mass is sufficiently large and active to ensure that the exit gas is substantially at equilibrium.

¹ A. F. Snowball, *Can. Chem. Process Inds.* **31**, 1110 (1947).

- (a) Calculate the temperature and composition of the gases leaving the converter.
 (b) If the gases leaving the converter are cooled to 400°C and fed to a second, similar converter, what are the temperature and composition of the gases leaving the second converter?

12. Compute in terms of pound mols of SO_3 produced per hour the maximum capacity of the system of Illustration 7 with each of the following methods of recycle:

- (a) From the outlet of the second converter to the inlet gas line of the first.
 (b) From the outlet of the first converter to the inlet gas line of the first.
 (c) From the outlet of the first converter to the inlet of the first, and from the outlet of the second to the inlet of the second.
 (d) From the outlet of the second converter, with part of the recycle gas being introduced into the feed line to the first converter and the rest into the discharge line from the first converter.

13. Compute the following quantities with the aid of Figs. 6-6 and 6-8:

(a) Btu evolved when 1 lb mol of pure H_2SO_4 at 100°F is mixed with 10 lb mols of pure H_2O at 100°F and the resulting solution is cooled to 100°F.

(b) Btu evolved when a solution of 90% acid, containing 1 lb mol of H_2SO_4 and initially at 80°F, is mixed with 10 lb mols of pure H_2O initially at 150°F and the resulting solution is cooled to 130°F.

(c) Btu evolved when 1 lb mol of pure H_2SO_4 at 90°F is added to a 30% acid solution containing 2 lb mols of H_2SO_4 and initially at 150°F, and the resulting solution is cooled to 150°F.

(d) Btu evolved when 100 lb of oleum at 100°F and containing 20% free SO_3 is diluted with sufficient 95% H_2SO_4 at 100°F to form 100% H_2SO_4 , and the product is then cooled to 100°F.

(e) The temperature of the 100% H_2SO_4 of part (d) before it is cooled.

(f) The temperature of the product when oleum at 100°F and containing 15% free SO_3 is fortified by the addition of SO_3 vapor at 150°F to make an oleum containing 25% free SO_3 , without loss of heat to the surroundings during the process.

(g) Partial pressure of SO_3 in mm Hg over 106.8% H_2SO_4 at 45°C.

14. A single absorption tower is to absorb SO_3 from a gas containing 12% SO_3 , fed at 64°F. Of the SO_3 in the feed gas, 50% is to be absorbed. The gas is to leave the tower at 70°F. The product from the tower will be 104.5% H_2SO_4 . Four volumes of acid are to be recycled for every volume withdrawn as product. Make-up water at 64°F will be fed to the recycle line. In addition, 98% acid at 150°F will be added to the recycle line at a rate such that it will provide one-third of the total SO_3 in the product. Coolers will be installed in the product line and in the recycle line just before it enters the tower to cool these streams to 64°F.

(a) Calculate the strength of acid (per cent free SO_3) entering the top of the tower.

(b) Calculate the temperature of the acid leaving the bottom of the tower. Can the tower operate as specified, so far as equilibrium limitations are concerned?

(c) On the basis of 100 lb mols of SO_3 entering the tower in the gas stream, compute the quantity of heat in Btu that must be removed in each cooler.

15. Using the same assumptions as those employed in the second trial of Illustration 10, with the exception that the rate of withdrawal of liquid from the bottom of each tower is to be 14,000 lb/hr instead of 16,000 lb/hr, prepare a complete flow sheet of the unit, showing all flow rates, concentrations, and temperatures.

16. A fertilizer company in the southeastern part of the United States has a contact sulfuric acid plant with the flow sheet shown in Fig. 6-16. The flow rates, temperatures, pressures, and concentrations entered on the flow sheet are average values over a 24-hr period during which the plant was operating smoothly and normally with

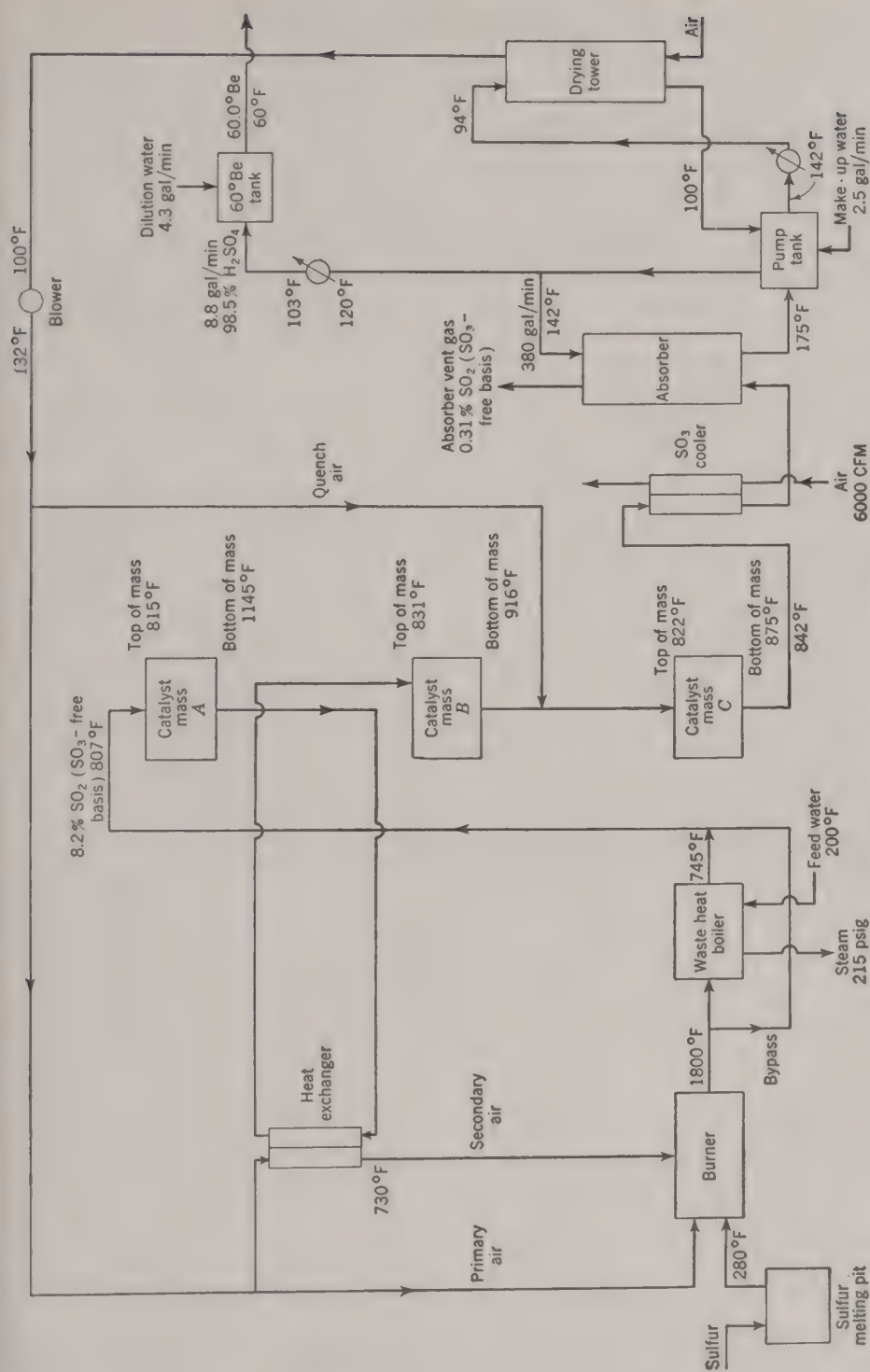


FIG. 6-16. Flow sheet for Prob. 16.

the catalyst in good condition. Estimate the following quantities as accurately as possible:

- (a) Per cent conversion of sulfur to H_2SO_4 .
- (b) Mols per hour of quench air.
- (c) Per cent of SO_3 in the burner gas.
- (d) Mols per hour of primary air.
- (e) Mols per hour of secondary air.
- (f) Pounds per hour of steam produced in the waste-heat boiler.
- (g) Composition of the liquid withdrawn from the bottom of the absorber.
- (h) The management is anxious to increase the output of this plant. However, an attempt to achieve this by increasing the sulfur feed rate, with a proportional increase in the supply of air, resulted in excessive entrainment of liquid spray in the vent gases leaving the top of the absorber. There is evidence to indicate that if something could be done about this "bottleneck" the rest of the system could take care of a somewhat higher throughput than the present one. List the various possible steps by which a higher output can be achieved, with your comments on each of the possibilities. What course of action do you recommend?

17. Information is available on a pyrrhotite burner in a New Hampshire paper mill.¹ The unit is of the fluidized-bed type, and mixing of the material in the bed is so complete that the temperature does not vary more than 20°F throughout the bed. The feed to this burner is a concentrate obtained by flotation from copper tailings. The concentrate is described as mainly pyrrhotite (Fe_7S_8), with minor impurities, and is reported to contain 8 to 10% water as received. More water is added to form a pumpable slurry, which is pumped continuously into the bed. Additional water is sprayed into the burner to control the temperature. The bed is fluidized by air supplied at the bottom, and the burner gas leaves at the top. Hot calcine is discharged continuously through an overflow pipe, while dust entrained in the gases is recovered by means of cyclone separators and a water scrubber. The overflow and cyclone products are quenched with water, mixed together, and conveyed to storage.

Average analyses of the feed and calcine are tabulated below. The iron oxide content of the calcine is described as being practically all magnetite (Fe_3O_4).

Constituent	Feed	Composite of overflow and cyclone product (97% of total calcine weight)	Scrubber solids (3% of total calcine weight)
Total S.....	35.7	0.51	1.5
Sulfide S.....	35.6	0.49	1.13
Total Fe.....	49.1	60.9	54.6
Ferrous Fe.....	42.5	16.8	18.9
Cu.....	0.61	0.74	1.3
Zn.....	1.03	1.41	2.8
Insolubles.....	8.1	8.3	14.3

Average flow rates and operating conditions are as follows: air flow, 3600 cu ft/min at 68°F and 1 atm; feed rate, 75 dry tons per 24 hr; feed slurry, 141 lb/min, containing

¹ R. B. Thompson, *Chem. Eng. Progr.*, **49**, 253 (1953).

73 wt-% solids; temperature-control water, 2.5 gpm; total water added to bed, 58 lb/min; temperature of fluidized bed, 1610°F; stack-gas analysis (dry basis), 13.0% SO₂, 0.2% SO₃, 1.0% O₂.

Test the above information for consistency in as many ways as possible, and state your opinion of the reliability of the data. Compute the heat in Btu per minute evolved by the reactions in the burner (considering both reactants and products to be in their standard states at 18°C); and determine what percentages of this heat are consumed as sensible heat in the calcine, sensible heat in the dry gas, vaporization and heating of water to gas temperature, and loss through the walls of the reaction vessel. In the light of the results, what kind of additional equipment do you think would be needed to secure a high recovery of the heat of reaction?

Chapter 7

NITROGEN COMPOUNDS

Synthetic ammonia. The great transformation brought about in the chemical industry by the appearance of synthetic ammonia just before the outbreak of the First World War may be difficult for the young engineer of today to comprehend. Cheap ammonia has been the basis of large-scale developments in the manufacture of such important products as fertilizer, explosives, and plastics, and in the United States alone production of synthetic ammonia is now well over 1,000,000 tons per year. Stoichiometric methods are of great value in analyzing the performance of the equipment used in the ammonia synthesis and in developing the maximum information from analytical data.

Illustration 1. The converter layout of a large synthetic-ammonia plant includes a first bank of eight converters in parallel, to which the gases from the feed-gas purification plant are fed through a common header. These converters discharge in turn into another common header, which leads to a cooling and condensing system in which liquid ammonia is condensed and from which it is removed. The dissolved gases in this liquid are removed by rectification, after reduction of pressure, and are then compressed and returned to the header leading from the converters to the condenser. The gas-free liquid ammonia from this operation is withdrawn as part of the plant product. A part of the gas mixture leaving the condenser is recycled to the feed header to the bank of eight converters. The rest of this gas flows to a second bank of two converters, which, with their own auxiliary condensing and recycling system, are operated similarly to the first eight. That portion of the gas from these two units that is not recycled through them flows to a final, single converter-condenser unit, which is again operated like the other two banks. The gas from this last converter that is not recycled back to it constitutes the purge gas from the whole system.

The total pressure, the temperatures at corresponding points, and other externally imposed operating conditions in the catalyst chambers, coolers, and condensers throughout the whole system described are substantially the same in all three banks. The recycle gases are handled by

booster pumps, which operate under pressure differentials that are relatively small compared with the total pressure on the system.

The gas mixture flowing to this system from the gas-purification plant contains on the average about 1% of unreacting gases (mainly argon plus methane). The concentration of these inert gases in the recycle line to the first bank of eight converters averages 5%. The ammonia content of the gases flowing through this bank of converters rises on the average from a value of approximately 3.5% at the entrance to the converters to 9% in the outlet line from them. The percentage of inerts in the gas purged from the final condenser of the whole system averages 25%. The ammonia in this purged gas is recovered by absorption in water.

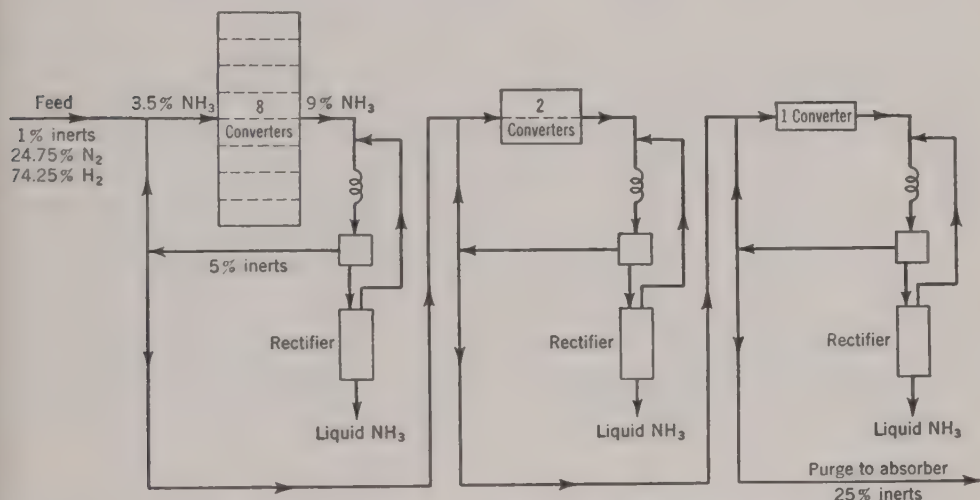


FIG. 7-1. Synthetic-ammonia plant of Illustration 1.

Every effort is made to keep the molal ratio of hydrogen to nitrogen essentially constant at 3:1. It is of course impossible to do this precisely, but controls are provided for prompt rectification of any deviations from this value, and, on the average, the effect of such deviations is negligible.

Calculate the following:

1. The percentage of the nitrogen and hydrogen entering the converter system as fresh feed from the gas-purification plant that is converted to ammonia in the first bank of eight converters.

2. The percentage yield of ammonia in the whole system, based on the nitrogen and hydrogen fed to it.

3. As a matter of operating experience, the plant has found that the mol fraction of inerts in the recycling gas in the middle bank of converters is approximately the geometric mean of the corresponding mol fractions in the first bank and in the final converter. On this basis, calculate the

percentage of the ammonia leaving the final converter as liquid ammonia and as dilute ammonia in the final purge gas.

4. Estimate the percentage of ammonia in the gases leaving the final converter and in the gases leaving the converters of the second bank, on the basis of the following considerations.

Where the catalyst in converters of this type is good enough, and where the gas is properly purified and its flow held to a rate that does not overload the unit, the catalyst will bring the gases to a pseudoequilibrium even though it will not bring them to complete chemical equilibrium. This is due to the fact that beyond this point the reaction rate, *i.e.*, the rate of final approach to full equilibrium, falls off to a negligible value. Because ammonia-synthesis gases deviate from the gas laws at the high pressures used, the equilibrium relationship does not conform to the ordinary expression for gas equilibrium until proper corrections for these deviations have been applied. However, so long as one is working at constant values of temperature and total pressure and the gas concentrations do not vary too widely, the square of the mol fraction of ammonia divided by the product of the mol fraction of the nitrogen times the cube of the mol fraction of hydrogen remains approximately constant under equilibrium conditions. (This would be the case if the gas laws held.) Moreover, the same is also true under a given set of conditions that develop the pseudoequilibrium described above, although of course the constant now has a different value from the true equilibrium one. Assume that this plant is operating under conditions of this sort.

Solution.

Basis: 100 mols fresh feed.

The flow sheet of the plant is shown in Fig. 7-1. In the first bank of converters let x = mol fraction NH_3 in recycle gas, n = mols net NH_3 withdrawn as liquid, and m = total mols recycled in the unit. The 100 mols of fresh feed contain 1 mol of inerts. Since the recycle contains 5% inerts, the purge from the first unit must equal $1/(0.05) = 20$ mols. By material balances (1) of ammonia around the mixing zone of the fresh feed and recycle gas streams, (2) of *total* nitrogen plus hydrogen around the whole first bank and its cooler-condenser system, and (3) of ammonia around the condenser unit,

$$\begin{aligned}xm &= 0.035(100 + m) \\99 &= 2n + 20(1 - x - 0.05) + 20(2x) \\(m + 20)(1 - x)(9/91) &= n + x(m + 20)\end{aligned}$$

In this last equation, $(m + 20)$ is the total gas leaving the condenser. Multiplying by $(1 - x)$ gives this gas on an ammonia-free basis. Multi-

plying by 9/91 gives the ammonia leaving the converter. Solution of the three equations gives $x = 0.04$, $n = 39.6$, and $m = 701$.

1. *Percentage conversion in first bank.*

$$100(2)[39.6 + 0.04(20)]/99 = 81.2\%$$

2. *Plant yield.* The final purge gas contains 25% inerts. Since 1 mol of inerts must be eliminated, the final purge equals 4 mols. Of this, 4% is NH_3 since, the noncondensable gases being so far above their critical temperatures, the change in the ratios of these gases from those in the gas from the first-bank condensers will not significantly change the fugacity and temperature of the ammonia in the gas mixture at the condenser outlet and hence will not change its concentration. The percentage of $\text{N}_2 + \text{H}_2$ is 71%, by difference. Hence,

$$[99 - 0.71(4) - 0.04(4)(2)]/99 = 96.8\% \text{ conversion}$$

3. *Percentage split in NH_3 leaving final converter.* The percentage inerts in the purge gas from the second converter is $\sqrt{5(25)} = 11.18\%$. Hence, by an inerts balance on the whole system up to the final converter-condenser unit, the total purge from the second unit is $1/0.1118 = 8.94$ mols, and since the NH_3 in this purge is 4%, the N_2 plus H_2 is

$$(1.0 - 0.04 - 0.1118)(8.94) = 7.59 \text{ mols}$$

The NH_3 is $(0.04)(8.94) = 0.36$ mol. The $\text{N}_2 + \text{H}_2$ in the purge from the third unit is $(0.71)(4) = 2.84$. Consequently

$$[7.59 + 2(0.36) - 2.84]/2 = 2.74 \text{ mols}$$

is the total NH_3 from the third unit. The gaseous NH_3 is

$$(0.04)(4) = 0.16 \text{ mol}$$

the rest, $2.74 - 0.16 = 2.58$ mols, is liquid. The per cent of the NH_3 leaving the third unit in the form of liquid is therefore

$$(2.58/2.74)100 = 94\%$$

4. *Percentage ammonia in the gases leaving the final converter and in the gases leaving the converters of the second bank.* In the purge from the first bank, the molal ratio of inerts to $(\text{inerts} + \text{N}_2 + \text{H}_2)$ equals $0.05/0.96 = 0.0521$. This must be the same as the ratio of inerts to $(\text{inerts} + \text{N}_2 + \text{H}_2)$ in the gases leaving the converters of the first bank. Therefore, the mol fraction of inerts in these gases is

$$0.0521(0.91) = 0.0474$$

the mol fraction of N_2 is $(0.91 - 0.0474)/4 = 0.2157$, and the mol fraction of H_2 is $0.91 - 0.0474 - 0.2157 = 0.6469$. Thus, the analysis of the

gases leaving the converters of the first bank is completely known, and one can calculate therefrom the value of the pseudoequilibrium constant, $(0.09)^2/(0.2157)(0.6469)^3 = 0.138$.

Let x , y , z , and u equal the mol fractions of NH_3 , N_2 , H_2 , and inerts, respectively, in the gases leaving the final converter. Four equations can be based on the facts that the sum of the mol fractions of the constituents must be unity; that the ratio of nitrogen plus hydrogen to inerts is unchanged by condensation of the ammonia by the particular technique employed; that the ratio of nitrogen to hydrogen is kept at 1:3; and that, under the converter operating conditions used, the pseudoequilibrium constant of the reaction should be the same as that in the gases from the converters of the earlier banks.

$$\begin{aligned}x + y + z + u &= 1 \\(y + z)/u &= (1 - 0.25 - 0.04)/0.25 \\z &= 3y \\x^2/yz^3 &= 0.138\end{aligned}$$

Solution of the equations for x gives the concentration of ammonia, 5.9%. By an entirely similar procedure, the ammonia concentration in the gases leaving the converters of the second bank is calculated to be 8.0%.

Ammonia oxidation. In the oxidation of ammonia, as in so many other operations, gas analysis alone provides significant information.

Illustration 2. An ammonia-oxidation unit using platinum-iridium catalyst discharges converted gases from the catalyst chamber through a heat exchanger for preheating the incoming air. It is desired to determine the conversion efficiency of the unit. To this end, a sample of the converted gases is withdrawn at the outlet of the heat exchanger, where the temperature of the gases has dropped to 515°F. The analysis of this gas can be reported in various ways. It is not uncommon to report the fixed nitrogen in terms of NO_2 and NO , evaluating these on the basis of the state of oxidation as analytically determined. However, this method of reporting is in large measure unrealistic because of the fact that the NO is in process of oxidation to NO_2 by the oxygen in the mixture itself, not only in its flow through the exchanger but also in the gas phase of the sampling flask itself before analysis is complete. The ratio as determined analytically is therefore dependent on the point in the equipment at which the sample is taken and on conditions of sampling and absorption that bear no relation to plant operation and performance. The really significant information afforded by the analytical procedure is the determination of the total fixed nitrogen in the original gas sample and the determination of what may be called the active oxygen. The latter is the sum of all the oxygen combined with nitrogen and that present in the form of oxygen gas which can combine with the fixed

nitrogen if this is present in sufficient amount and suitable opportunity for combination is afforded. Active oxygen does not include any oxygen in the form of water, because such oxygen is not available for nitrogen oxidation. In any event, the results must be reported on a suitable basis; 100 mols of N_2 is probably best for this purpose.

In the case being considered, the analyst elected to report his results in still a third way. He took the analytical data and calculated what the gas analysis would have been on the basis of three purely hypothetical and indeed unrealistic assumptions: (1) that the gas sample be allowed to stand long enough so that all NO would oxidize to NO_2 but no further, (2) that no fixed nitrogen would condense out of the gas despite the presence of the water, and (3) that the NO_2 would be present in the gas as such and none of it as N_2O_4 . On this basis he reported 11.2% NO_2 , 2.2% O_2 , and 86.6% N_2 .

Calculate the conversion efficiency of the catalyst unit and the percentage of ammonia (dry basis) in the ammonia-air mixture entering the catalyst chamber.

Solution.

Basis: 100 mols of dry gas reported by analysis.

This contains 11.2 atoms of fixed nitrogen and 26.8 atoms of active oxygen. Call m the mols of NH_3 and n the mols of dry air. First set up an oxygen balance around that part of the equipment preceding the point of gas sampling. Knowing that all the hydrogen from the ammonia will appear as water, $2(0.21)n = 26.8 + 1.5m$. Then by a total nitrogen balance,

$$m + 2(0.79)n = 2(86.6) + 11.2$$

Hence, $n = 108.7$, $m = 12.6$, and the conversion efficiency, which is the per cent of the ammonia appearing as fixed nitrogen, is

$$100(11.2/12.6) = 88.9\%$$

The per cent ammonia in the entering gases

$$= 100(12.6)/(108.7 + 12.6) = 10.4\%$$

Alternatively, 1 mol of NH_3 fed to the unit can be taken as a basis. Let x = atoms of fixed nitrogen resulting from it and y = mols of air used. By an oxygen-hydrogen balance, $2(0.21)y = 26.8x/(11.2) + 1.5$. By a nitrogen balance, $2(0.79)y + 1 = x + 2x(86.6)/(11.2)$. Hence, $x = 0.889$, $y = 8.62$, and the conversion efficiency = 88.9%. The ammonia percentage in the ammonia-air mixture entering is

$$100/(1 + 8.62) = 10.4\%$$

Still a third approach could be used. Taking 1 mol of NH_3 as a basis, let x = mols air and y = mols converter gas. Then, by an oxygen balance, $2(0.21)x = 2(0.134)y + 1.5$, and by a total nitrogen balance $1 + 2(0.79)x = 0.112y + 2(0.866)y$. Thus, $x = 8.62$, $y = 7.94$, and the conversion efficiency is $(0.112)(7.94)(100) = 88.9\%$. The percentage of ammonia in the entering air-ammonia mixture is

$$100/(8.62 + 1) = 10.4\%$$

It will be noted that these are not independent methods of calculation but merely three different arrangements of the same data according to

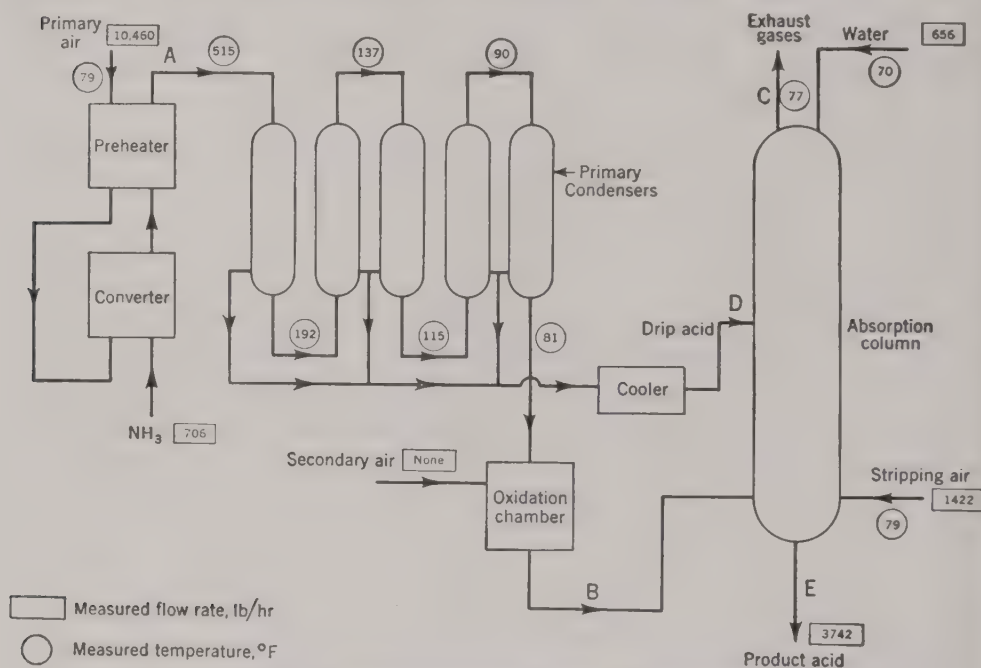


FIG. 7-2. Ammonia-oxidation plant of Illustration 3.

the basis selected for calculation, and of course they lead to identical results.

The engineer in industry is frequently faced with situations in which he has plant data that are obviously important but of limited accuracy and doubtful dependability. He is tempted to conclude that the thing to do in these situations is to discard the data that he has and obtain a new set of truly good data. However, it is often impracticable to do this with the time and facilities available, particularly when it is necessary to avoid interference with plant production schedules. In these situations, then, the engineer must make a careful analysis of the data that he has in order to determine their dependability before using them in the solution of the varied problems of plant control which the process

industries constantly face. The following problem on ammonia oxidation is intended to illustrate the technique of using material balances to evaluate the dependability of plant data.

Illustration 3. Test information has been obtained on the operation of one unit of an ammonia-oxidation plant, using Pt-Ir catalyst, to analyze the plant performance when that unit was running without the usual introduction of secondary air into the stream of converted gas beyond the primary condensers, before its flow to the final absorbing column. Figure 7-2 is a flow sheet, showing all flow rates that can be measured directly. The operating pressure was 107 psig.

The table below gives average analyses of various streams. The gas analyses are reported as ratios of fixed nitrogen and of active oxygen to nitrogen gas (N_2 plus inerts).

GAS ANALYSES

Basis: 100 mols N_2 in the sample.

Point of sampling	A	B	C
Atoms of fixed N.....	13.5	10.1	0.083
Atoms of active O.....	26.7	18.3	6.89

LIQUID ANALYSES
Weight per cent

Point of sampling	D (drip acid)	E (product)
HNO_3	49.9	63.6
NO_2	2.9	0.15
H_2O (by difference).....	47.2	36.25

The liquid-flow rates are believed to be quite dependable. The air-flow rates were measured by uncalibrated orifices, and the test report itself points out that these may be in error, conceivably (though improbably) by as much as 10%.

It is desired to use these data to determine the efficiency of conversion of ammonia to nitrogen oxides in the catalyst unit, the efficiency of recovery of these nitrogen oxides as liquid products, and the distribution of these oxides between liquid and gas streams at the point where they leave the cooling system and enter the final tower.

Solution. The first thing to do is to size up the over-all performance of the unit. Inspection of the flow sheet shows that no data are given on the flow rate of the exhaust gases. Consequently, the dependability of the data cannot be tested directly by setting up any sort of over-all balance. However, the exhaust-gas flow rate can be computed by a

suitable balance; moreover, there are three elements on which data are available, so that theoretically the unknown flow rate can be computed by a balance based on any one of the three. For setting up these balances, the analyses of the streams must be expressed in terms of the elements. The analysis of the liquid product is converted to this form by the conventional technique in the table below.

Basis: 100 lb product acid.

Component	Pounds	Mols	Atoms N	Atoms H	Atoms O
HNO ₃	63.6	1.010	1.010	1.010	3.030
NO ₂	0.15	0.003	0.003	0.006
H ₂ O.....	36.25	2.015	4.030	2.015
Total.....	100.0	3.028	1.013	5.040	5.051

The air supply to the unit must have been cooled after compression and is presumably saturated with water vapor. In view of the conditions of gas-liquid contact of the exhaust gases just before leaving the system, that gas also must be substantially saturated. Consequently, the analyses of the gas streams must be corrected for the moisture content which, although small, is not negligible. This is done below.

The partial pressure of water vapor in the entering air is 1.0 in. Hg. Since the total pressure is 121.7 psia, or 247.5 in. Hg, the ratio of vapor to dry air, neglecting gas-law deviations, is $1/246.5 = 0.00405$. Since a mol of air contains 0.42 atom of oxygen, the total oxygen per mol of dry air is 0.424. The number of atoms of hydrogen on the same basis is 0.0081.

The exhaust gas presents a complication because the state of oxidation of its fixed nitrogen is uncertain. It could be present as NO, NO₂, N₂O₄, or conceivably even as a dilute acid fog, or as some mixture of all four. The fact is that the amount of fixed nitrogen is so low that its condition is quite unimportant in determining the amount of water vapor in the gas. Assuming all of it to be present as NO₂,* the total mols of dry exhaust gas per 100 mols of N₂ is

$$0.083 \text{ mol NO}_2 + 0.5[6.89 - 2(0.083)] \text{ mols O}_2 + 100 \text{ mols N}_2 = 103.34$$

Since the vapor pressure of water is 0.93 in. Hg, the ratio of H₂O to dry gas is $0.93/(247.5 - 0.9)$ and that of H₂O to N₂ is $103.34/100$ times this, or 0.0039. Hence, the ratio of total oxygen to N₂ is

$$0.0689 + 0.0039 = 0.0728$$

while that of atoms of hydrogen to N₂ is 0.0078.

* The dissociation of N₂O₄ would be considerable on account of the low partial pressure.

With these results the hourly quantity of exhaust gases may now be calculated. It is desirable to give the flow rate of these gases as mols per hour of N_2 gas present as such (which is the total nitrogen less the fixed nitrogen). The reason for doing this is not only that the composition of these gases has been expressed on the basis of this N_2 but also that it is an unchanging quantity, offering a fixed base because it takes no part in the complicated reactions occurring in the system. Table 7-1 sets up three total element balances, nitrogen, oxygen, and hydrogen. In each balance, the quantity of the element in question appearing under the heading "exhaust gas" is found by difference. The unknown flow rate of the nitrogen in the exhaust gas itself, which is to be calculated, is designated x mols/hr. However, the numerical value that will be obtained for x will depend upon the element balance taken.

First use a nitrogen balance. Each 100 mols of N_2 carry 0.083 atom of fixed nitrogen. Hence, the fixed nitrogen is $0.083/200.083$ times the total nitrogen, 650.0 atoms, or 0.27 atom. Consequently, the flow rate of molecular N_2 is $650.0 - 0.3 = 649.7$ atoms/hr, or $x = 325$ mols/hr.

A total oxygen balance combined with the exhaust gas analysis gives $x = 21.2/0.0728 = 291$ mols N_2 per hour. Similarly, a hydrogen balance gives $x = 11.9/0.0078 = 1526$ mols nitrogen per hour. The last of these is obviously likely to be subject to gross error, because (1) the hydrogen in the exhaust gas calculated by difference is less than 6% of the total hydrogen flowing through the system, and (2) the hydrogen in the exhaust gas is very small and was estimated and not measured. The flow rate

TABLE 7-1. ELEMENT BALANCES ON AMMONIA OXIDATION

Basis: 1 hr.

Stream	Amount	Atoms N		Atoms O		Atoms H	
		In	Out	In	Out	In	Out
Total air (dry) . .	409.7 mols	647.3	173.7	3.32	
Ammonia	706 lb	41.5	0	124.5	
Water	656 lb	0	36.45	72.9	
Product acid	3742 lb	38.0	189.0	188.8
Exhaust gas	x mols N_2	650.0	21.2	11.9
Total	688.8	688.8	210.2	210.2	200.7	200.7

calculated by the hydrogen balance should clearly be thrown out. The calculation based on the oxygen balance is subject to the same objections as those leveled against the hydrogen balance, but in far less degree. However, the nitrogen balance is obviously the most dependable for determining the exhaust-gas flow rate x . In other words, one would be inclined to accept the nitrogen-balance flow rate or perhaps to average it

with the oxygen-balance flow rate, giving the former considerably greater weight in arriving at the proper average.

An approach alternative to a total oxygen balance is a balance based on active oxygen, which was defined in Illustration 2 as oxygen in the form of nitrogen oxides plus the oxygen available for oxidizing them. Actually, this is total oxygen less oxygen present as water or equivalent to hydrogen in nitrogen compounds (NH_3 and HNO_3). The total oxygen entering the system other than that as water or water vapor is the oxygen in the dry air, 172.0 atoms. In the converter $1.5(41.5) = 62.25$ atoms of this oxygen goes to water, leaving 109.8 atoms of active oxygen in the converted gases. The total oxygen in the acid product is 189.0, but the equivalent of hydrogen in this acid, which is 94.4 atoms, must be subtracted, leaving 94.6 as the active oxygen in the product. This leaves 15.2 atoms of active oxygen by difference in the exhaust gas, corresponding to a nitrogen-flow rate of $15.2/0.0689 = 241$ mols/hr. This method of calculation eliminates any effects of water, either in the entering air or in the exhaust gases. The result should consequently be more dependable than that from the total oxygen balance. It is surprising to find it so far below the result of the nitrogen balance. However, the nitrogen balance in Table 7-1 shows that the nitrogen exhaust gas comes almost exclusively from the air, the measured flow rate of which is admittedly open to question. The liquid-flow rates, determined presumably by weighing, gauging, or equivalent methods, ought to be by far more dependable than gas-orifice readings. In the nitrogen balance, these liquid-flow rates are given practically no weight at all. Is it possible to calculate the flows on the basis of liquid-flow-rate data alone?

This can be done by ignoring the measured air-flow rate and treating it as unknown. Call the total air-flow rate m and the exhaust- N_2 rate n mols/hour. It is now possible to set up three balances based on nitrogen, oxygen, and hydrogen. However, for determining the gas-flow rates the hydrogen balance will be completely unreliable because of the small amount of total hydrogen present in the air and exhaust-gas streams and the uncertainty of their hydrogen contents. Setting up the nitrogen and total oxygen balances, one obtains

$$\begin{aligned} 1.58m + 41.5 &= 38.0 + 2.0008n \\ 0.424m + 36.45 &= 189 + 0.0728n \end{aligned}$$

Hence,

$$m = 416 \quad n = 331$$

Similarly, using nitrogen and active oxygen balances,

$$\begin{aligned} 1.58m + 41.5 &= 38.0 + 2.001n \\ 0.42m - 62.25 &= 94.6 + 0.0689n \end{aligned}$$

Hence,

$$m = 429 \quad n = 341$$

Because these calculated gas rates are based on measured liquid rates only, the probability of their dependability is high. Moreover, because the active oxygen balance involves no assumptions as to the water contents of the gas streams, the rates calculated by using it are the more dependable of the two sets of values and probably the most dependable of any so far computed. It will be noted that this calculated air rate, 429 mols/hr, differs by less than 5% from the measured air rate reported in the test, 409.5 mols/hr.

One can use a hydrogen balance in combination with either nitrogen, total oxygen, or active oxygen balances, but as indicated above, one would not expect it to be at all dependable. In fact, the first combination gives a negative result and the last two give results that are impossibly high numerically. The last combination of the six combinations available, *i.e.*, the total oxygen and active oxygen balances, is clearly undependable because it will involve small differences in the two equations that might easily introduce gross error in the final results. In fact, the nitrogen-flow rate thus calculated turns out to be 175.0 mols/hr.

Summing up the calculations to this point, good judgment seems to indicate that the best values of the gas-flow rates are 429 mols/hr for the total entering air and 341 mols of N_2 per hour in the exhaust gas.

The yield of product acid as a percentage of the ammonia fed is $(38.0/41.5)100 = 91.6\%$. This value is obviously independent of the gas-flow rates. The loss of fixed nitrogen unabsorbed is

$$3.41(0.083) = 0.283 \text{ atom/hr}$$

which is 0.68% of the original ammonia fed to the system.¹

The chemical-conversion efficiency of ammonia to fixed nitrogen in the catalyst unit is therefore 92.3%, and the per cent absorption of the fixed nitrogen converted to oxides in the catalyst unit is 99.25. The mols of N_2 per hour formed by the oxidation of the ammonia is

$$41.5(0.077)/2 = 1.6.$$

The hydrogen lost in the exhaust gas is $341(0.0078) = 2.66$ atoms/hr. This means that the hydrogen unaccounted for is $11.9 - 2.7 = 9.2$ atoms/hr, which, in a total of 200.7 atoms flowing through the system, is 4.6% failure of closure of the hydrogen balance. This 4.6% is a good measure of the probable uncertainty of the over-all flow-rate figures.

Now attention may be focused on the converted gas leaving the pre-heater. There are 13.5 atoms of fixed nitrogen per 100 mols of N_2 in it.

¹ It should be noted that this value is higher than would have been obtained from any of the dependable values of nitrogen-flow rates calculated by other balances. In this sense, the figure is conservative.

Since the over-all data indicate a conversion efficiency of 92.3%, the NH_3 oxidized was $13.5/0.923 = 14.63$ atoms, of which 7.7% went to form 0.564 mols N_2 . The remaining N_2 , 99.44 mols, presumably came in as air, bringing $(42/79)(99.44) = 52.83$ atoms of oxygen with it. However, inasmuch as the evidence available indicates that platinum-iridium catalyst converts all the hydrogen of ammonia to water, $1.5(14.63) = 21.95$ atoms of this oxygen were thus consumed, leaving $52.83 - 21.95 = 30.88$ atoms of active oxygen. This is 15.7% more than the 26.7 atoms reported by analysis. The discrepancy seems excessive.

Another approach is to calculate the conversion efficiency of the ammonia to fixed nitrogen from the data of this same gas analysis by the method of the preceding illustration, *i.e.*, by the use of element balances around the whole of that part of the unit ahead of the point of gas sampling. The result is 79.3%. This contrasts with the 91.6% yield of product that was actually recovered and measured and with the 92.3% conversion computed for over-all performance, both based on the directly measured liquid ammonia consumed. The analysis of the converted gas from the preheater is evidently so seriously in error that it is unwise to try to use it in interpretation of plant performance.

Turning to the analysis of the oxidation-chamber gas, this must be interpreted in the light of the drip acid which has been condensed out of it and with which it is presumably in substantial equilibrium. The accompanying breakdown of the drip-acid analysis shows an atomic ratio of H/N of 6.031/0.854, or 7.06. This large amount of hydrogen comes mainly from the ammonia, since the amount in the primary air is small in comparison. It is true that the moisture content of the oxidation-chamber gas is lowered, despite its somewhat higher temperature, by its

TABLE 7-2. ANALYSIS OF DRIP ACID

Basis: 100 lb drip acid.

Component	Pounds	Mols	Atoms N	Atoms H	Atoms O
HNO_3	49.9	0.791	0.791	0.791	2.373
NO_2	2.9	0.063	0.063	0.126
H_2O	47.2	2.62	5.24	2.62
Total.....	100.0	3.474	0.854	6.031	5.119

lower volume as well as by the lowering of the vapor pressure of water by the nitric acid in the condensed drip. There will be little error in estimating the amount of the drip by a hydrogen balance, neglecting any condensation of the water vapor entering in the primary air.

It should be obvious that the way to study the streams entering the absorption tower is to take a section through the equipment just prior

to the tower and set up balances at that section. These balances can be taken either around the tower or around the whole of that part of the system before the tower. The exhaust gas from the tower was not measured, and while it is true that its value has been calculated from over-all balances, one would prefer balances based only on directly measured quantities. Both streams entering that part of the system prior to the tower were measured, so it is practicable to set up such balances here. For this purpose, Table 7-3 is self-explanatory.

TABLE 7-3. AMMONIA OXIDATION PLANT UP TO ABSORPTION TOWER
Basis: 1 hr.

Stream	Flow rate	Atoms H	Atoms O	Atoms N (total)
Primary air (dry).....	361 mol/hr	0	151.9	570
NH ₃	41.5 mol/hr	124.5	0	41.5
Drip acid.....	x lb/hr	$0.06031x$	$0.05119x$	$0.00854x$
Oxidation-chamber gas.....	y mol/hr N ₂	0	$0.183y$	$2.101y$

Data are available for three balances—nitrogen, oxygen, and hydrogen. There are only two unknowns, namely, the quantities of drip acid and oxidation-chamber gas. There are, therefore, three solutions possible, each based on two of these balances.

Granting that any net condensation from the gas stream of the water vapor in the entering air may be neglected, the drip acid can be calculated directly by a hydrogen balance and is found to be 2063 lb. This means that the amount of the oxidation-chamber gas stream, expressed in mols of nitrogen gas, can now be calculated directly either by an oxygen balance or by a nitrogen balance. The results are given in the first two columns of figures in Table 7-4.

TABLE 7-4. SOLUTION TO TABLE 7-3

	H and O balance	H and N balance	N and O balance
Drip acid, x lb/hr.....	2063	2063	1955
Oxidation-chamber gas, y mol/hr N ₂	253	283	284
Per cent conversion.....	104.1	111.4	109.5

Alternatively, one can ignore hydrogen and calculate the quantities of drip acid and oxidation-chamber gas by the simultaneous equations corresponding to the nitrogen and oxygen balances. The results are in the third column of figures of Table 7-4.

In view of the nature of the data, the differences in the results do not look excessive. However, there is another way in which the results can be interpreted. Using the calculated flow rates, one may calculate from the analytical data the fixed nitrogen in each stream and from this the chemical conversion. These conversions are shown in the last line of Table 7-4.

From the known chemistry of the process, conversion efficiencies above 100% are impossible. However, excessive efficiencies are indicated by all three of the pairs of balances employed to interpret the data. Moreover, these efficiencies are completely out of line with those obtained above from the over-all balances on the plant. There must be something fundamentally wrong with the data.

For each of these three pairs of balances one can now calculate the error (*i.e.*, lack of closure) in the third element balance not used in the solution. When hydrogen and oxygen balances were used in computation, the nitrogen balance is found to be off by 10.1% *excess of input* over output; the hydrogen-nitrogen balance results give, for oxygen, 3.6% *excess of output*; the nitrogen-oxygen balance gives, for hydrogen, 5.2% *excess of input*.

From a balance around the whole of that part of the system prior to the absorption tower, the hydrogen from ammonia is 124.5 atoms per hour (see Table 7-3), whence the drip acid is $124.5(100)/6.031 = 2063$ lb. It contains $20.63(0.854) = 17.63$ atoms of fixed nitrogen. Since from the over-all balances the total fixed nitrogen formed is $41.5(0.923) = 38.3$ atoms, the remaining 20.67 atoms must be in the gas. Hence, the N_2 in the gas is $20.67/0.101 = 204.5$ mols. Of this, $41.5(0.077)/2 = 1.6$ mols come from NH_3 , leaving 202.9 mols from air. This N_2 brings in

$$(42/79)(202.9) = 107.9 \text{ atoms}$$

of oxygen with it. However, there are $20.63(5.119) = 105.6$ atoms of oxygen in the drip, leaving only 2.3 atoms in the gas. The ratio of this to N_2 , $2.3/204.5 = 0.0112$, is so far out of line with the figure reported by analysis, 0.183, that here also there is clearly something fundamentally wrong with the analytical data. Whether the trouble is with analysis of drip acid or with that of gas is uncertain. It seems more likely that the gas analysis is off, because the technique of that analysis, both sampling and analysis itself, is so much more sensitive to errors than that of the drip acid.

It appears that, whereas the data on the over-all performance of the unit are consistent within about 5% in the element balances and correspondingly dependable, the analytical data within the cooler-condenser system are too inconsistent within themselves and in relation to the over-all figures to justify giving them consideration.

Nitric acid. Concentrated nitric acid is normally made by distilling the product of ammonia oxidation in the presence of strong sulfuric acid, which acts as a dehydrating agent. However, reaction of nitrate with sulfuric acid continues to be an important source of nitric acid in certain areas. The final illustration of this chapter deals with some practical aspects of the latter method.

Illustration 4. A chemical plant is manufacturing nitric acid from nitrate and sulfuric acid. The procedure is to charge a pot still with the reactants, heat the still, and drive the nitric acid vapors overhead to a system of condensers until reaction ceases and the still can be emptied and recharged. The standard charge is 2000 lb of nitrate and an equal weight of 66°Bé sulfuric acid. On a dry basis, the nitrate averages 96% NaNO_3 . However, the nitrate as weighed before charging to the still contains some moisture. Along with the nitric acid, water from the nitrate and the sulfuric acid is distilled from the pot. This appears in relatively large quantities as dilute acid in the initial and final stages of each run. However, the acid recovered during the middle portion of the run is quite concentrated.

For some time, the plant has had a favorable market for the sale of 95% HNO_3 , whereas weaker acids bring considerably lower prices. The stream of acid leaving the condensing system is sent to the 95% HNO_3 storage tank during the middle portion of each run. During the initial and final stages, the stream is diverted to weak-acid storage. The exact point in the distillation at which the stream is shifted from one tank to the other is left to the discretion of the operators. Their instructions are to cut the distillate stream into the strong-acid tank at some time within a half hour to an hour after the first signs of distillate in the condenser sight box, following the start of a run. After the peak of the evolution of distillate has passed and the stream becomes increasingly dilute, samples are taken from the strong-acid tank from time to time, and when analysis shows that the concentration has dropped to 95% HNO_3 , the distillate stream is switched back to weak-acid storage.

An engineer in the employ of this company has pointed out that it should be possible to increase the yield of 95% HNO_3 from each run by more judicious choice of the "cut points." In order to provide a basis for analyzing the situation, a series of tests have been conducted, in which information has been secured on the progress of distillation during several runs. The averaged data are given in Table 7-5.

It has been found that the data points for an individual run fall quite close to the average curve if the data are plotted as C vs. W . On the other hand, a scattering of the points is evident if C is plotted against θ . For this reason, C and W are chosen as the coordinates of Fig. 7-3.

On the assumption that you have been delegated to go over the above

TABLE 7-5. NITRIC ACID DISTILLATION

θ = time from start of run, hr
 W = total weight of HNO_3 and H_2O distilled up to time θ , lb
 C = weight fraction of HNO_3 in acid being evolved at time θ

θ	W	C	θ	W	C
0	0	0.608	2.50	855.3	0.956
0.25	22.7	0.654	2.75	905.3	0.952
0.50	33.5	0.674	3.00	1049	0.934
0.75	61.5	0.728	3.25	1115	0.917
1.00	187.1	0.976	3.75	1255	0.872
1.25	347.8	0.973	4.25	1304	0.851
1.50	513.3	0.969	4.75	1354	0.823
1.75	713.3	0.963	5.25	1423	0.769
2.00	761.3	0.961	5.75	1526	0.673
2.25	809.3	0.959	7.25	1710	0.640

information and report on it, analyze the data and prepare a summary of the material that should be included in your report.

Solution. Before becoming immersed in detailed calculations, it is wise to review the over-all problem of how to control the "cut points." The fact that the data correlate imperfectly on a time basis means that

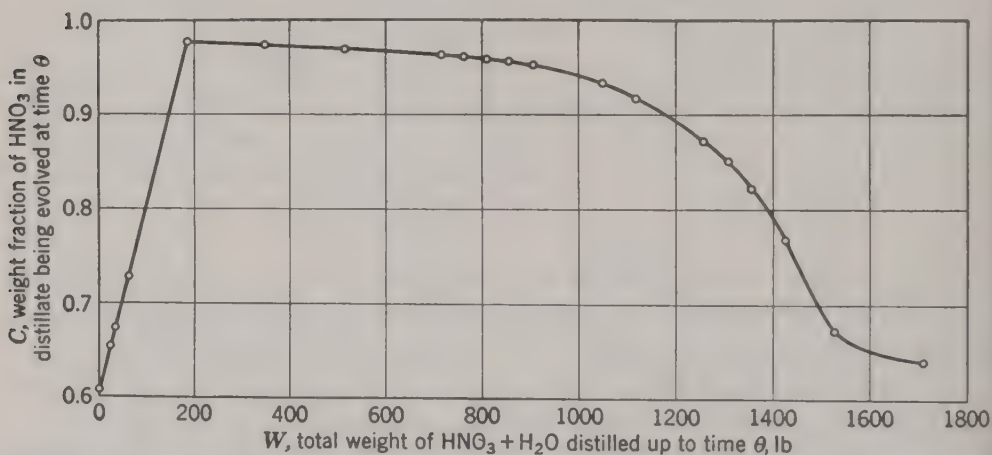


FIG. 7-3. Variation of acid strength during distillation of nitric acid from nitrate and sulfuric acid.

the rate of distillation varies to some extent from one run to the next. Hence, control of the initial "cut point" on a time basis is not very satisfactory from the angle of getting reproducible results. Control of the final "cut points" by the analysis of samples from the strong-acid tank is open to the objection that this tank is filled with acids of varying strengths, which are probably not completely mixed, thus making it

difficult to get a sample that is truly representative of the whole contents. Measurement of weights, as done in the tests on the unit, involves too many complications for daily use by the plant operators. The best method is to depend on analyses of spot samples of the distillate stream since these can be made rapidly and accurately, with simple equipment.

If the operator is to be told to make the first "cut point" at one acid strength and the second at another, is there any simple relationship between the two which will help to simplify the instructions? A little reflection will show that there is. For maximum production of acid of a given strength, the operator should make his initial and final cuts at the same acid strength. Suppose, for example, that the initial and final "cut points" are both at 87% HNO_3 , giving (as will be shown later) a strong-acid cut averaging 95% HNO_3 . If the initial cut is made at some concentration below 87%, the effect is to add to the mixture a certain amount of acid weaker than 87%. If the average concentration of the strong-acid cut is to remain 95%, the effect of the first change must be counterbalanced by moving the second "cut point" to a concentration somewhat higher than 87%. Thus, acid stronger than 87% is subtracted from the mixture and acid weaker than 87% is added. Since weaker acid always has a greater diluting effect than stronger, the addition of a relatively small amount of weaker acid has a dilution effect that can be counterbalanced only by subtraction of a somewhat larger amount of stronger acid. The net effect, then, is a reduction in the weight of the 95% cut, and the conclusion is inescapable that the maximum yield of 95% acid occurs when both "cut points" are at 87% HNO_3 .¹ If it is desired to produce a strong acid cut with an average concentration other than 95%, a similar argument applies.

¹ This conclusion is also reached if the process is visualized as being carried out in the following way. Suppose that the weak acid produced in the first part of the run is collected in a series of small tanks, the cut into each tank being made at each 1 per cent increase in the strength of nitric acid. When the strength reaches 95%, all acid above that strength is cut into one large "strong-acid" tank until the strength again falls to 95%. Then, at each 1 per cent change going down, other cuts are made. Since there is no essential difference between a dilute acid fraction going up and another of the same strength going down, like fractions go into the same tank. At the end of the run there is a large tank of acid averaging somewhat over 95% and a series of fractions of lesser strength each differing by 1 per cent. Now if it is desired to make 95% acid by blending acid in the "strong-acid" tank with the dilute fractions, the way to get maximum production of 95% is to blend the strong acid first with 94%, then with 93%, and so on, until the total blended acid tests 95%, never using an acid of low strength until all fractions of higher strength have been used. In this way the "strong acid" is stretched out to make the greatest amount of 95% acid. Since the last fraction used in making the blend contains weak acid made going up as well as weak acid of the same strength made coming down, *i.e.*, fractions made at the same "cut point," it follows that the "cut point" to make the greatest production of 95% (or any other per cent) must be the same in both directions.

The next step is to establish the acid strength at which the operators should switch into and out of the strong-acid storage, in order to produce 95% HNO_3 . As a matter of foresight, it is advisable to determine the proper "cut points" for production of other strengths of acid as well, since variation in market conditions may at any time make it profitable to manufacture an acid of different strength. It is also apparent that the relation between the strength of acid produced and the yield is of great importance in economic calculations.

The production of a cut from acids of varying strengths evolved at different stages of the distillation is obviously a problem in integration. However, it may not be immediately evident that the integral of the curve through the points on a plot of the data has physical significance in relation to the problem. The only safe procedure is to consider first a differential step of the process.

In a differential element of time $d\theta$, during which dW lb of distillate are evolved, the weight of HNO_3 produced is $C dW$ and the weight of H_2O is $(1 - C) dW$. During the period from the start of the run to time θ , the weight of HNO_3 distilled is the integral $\int_0^W C dW$, while the H_2O is equal to $W - \int_0^W C dW$. Since Fig. 7-3 is a plot of C against W , the area under the curve, between $W = 0$ and $W = W$, is equal to $\int_0^W C dW$ and is a graphical representation of a physical quantity, *i.e.*, the weight of HNO_3 distilled in the interval. The area between the curve and the line $C = 1$ represents the weight of H_2O distilled. By contrast, if the data had been plotted in another way, *e.g.*, as C against θ , the area under the curve would then have had no physical significance relevant to solution of the problem.

The results of graphical integration of Fig. 7-3 may be presented either as pounds of HNO_3 or as pounds of H_2O distilled vs. the total pounds distilled. However, the amounts of H_2O are relatively small compared to the HNO_3 produced, and hence large percentage variations in the concentration of H_2O in the distillate lead to comparatively small percentage variations in the concentration of HNO_3 . The consequence is that a plot of pounds of HNO_3 tends to mask what may be large percentage effects with respect to H_2O . As a general rule, it is preferable to focus on the impurities in a mixture (H_2O in this case), as a more sensitive index of the behavior of the mixture than the principal constituent. In line with this principle, the results of integrating the curve of Fig. 7-3 are given in Fig. 7-4 as pounds of H_2O distilled versus the total pounds distilled.

At the end of the distillation ($W = 1710$), the curve of Fig. 7-4 shows that the total amount of water evolved is 210 lb. By difference, the

total amount of HNO_3 is $1710 - 210 = 1500$ lb. Comparison of these figures with the amounts one would predict on the basis of the charge serves as a valuable check on the dependability of the data as a whole. If one neglects moisture in the charge, the input of NaNO_3 is

$$2000(0.96)/85 = 22.6 \text{ lb mols}$$

Standard 66°Bé sulfuric acid contains 93.19% H_2SO_4 , making the input of H_2SO_4 equal to $2000(0.9319)/98 = 19.0$ pound mols. The production of HNO_3 amounts to $1500/63$, or 23.8 lb mols. The principal reaction occurring in the still is $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$, followed

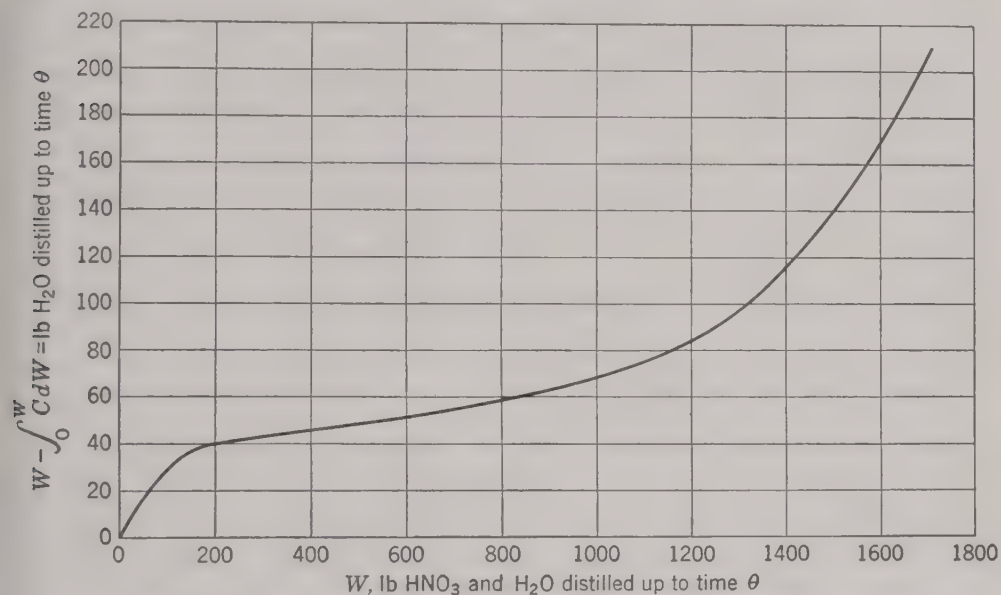


FIG. 7-4. Amount of water distilled vs. total amount of distillate.

by the second reaction $\text{NaNO}_3 + \text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{HNO}_3$. Granting complete reaction of the nitrate, the number of mols of HNO_3 produced should equal about 95% of the number of mols of NaNO_3 , since about 5% of the nitrogen goes to lower nitrogen oxides. The degree of agreement between the nitrogen input and output is satisfactory, in view of the probable accuracy of weighings and sampling under plant conditions. It is also possible to check on the water balance. The water content of the sulfuric acid is $2000(0.0681) = 136$ lb, leaving $210 - 136$, or 74 lb, derived from moisture in the nitrate. This is a reasonable amount.

Figure 7-4 offers a convenient means of determining the interrelation of "cut point," the average strength of the strong-acid cut, and the yield. Suppose that one chooses to make the initial and final cuts at 90% HNO_3 . From Fig. 7-3, it is seen that these points correspond to $W = 150$ and

$W = 1180$. The yield is $1180 - 150 = 1030$ lb. Reference to Fig. 7-4 shows that when $W = 150$, the water distilled up to that time is 37 lb. When $W = 1180$, 82 lb of H_2O have been distilled. By difference, the water in the cut is $82 - 37 = 45$ lb. This means that the weight fraction of water in the cut is $45/1030 = 0.044$. Therefore, if the "cut point" is 90%, the yield is 1030 lb and the average composition of the

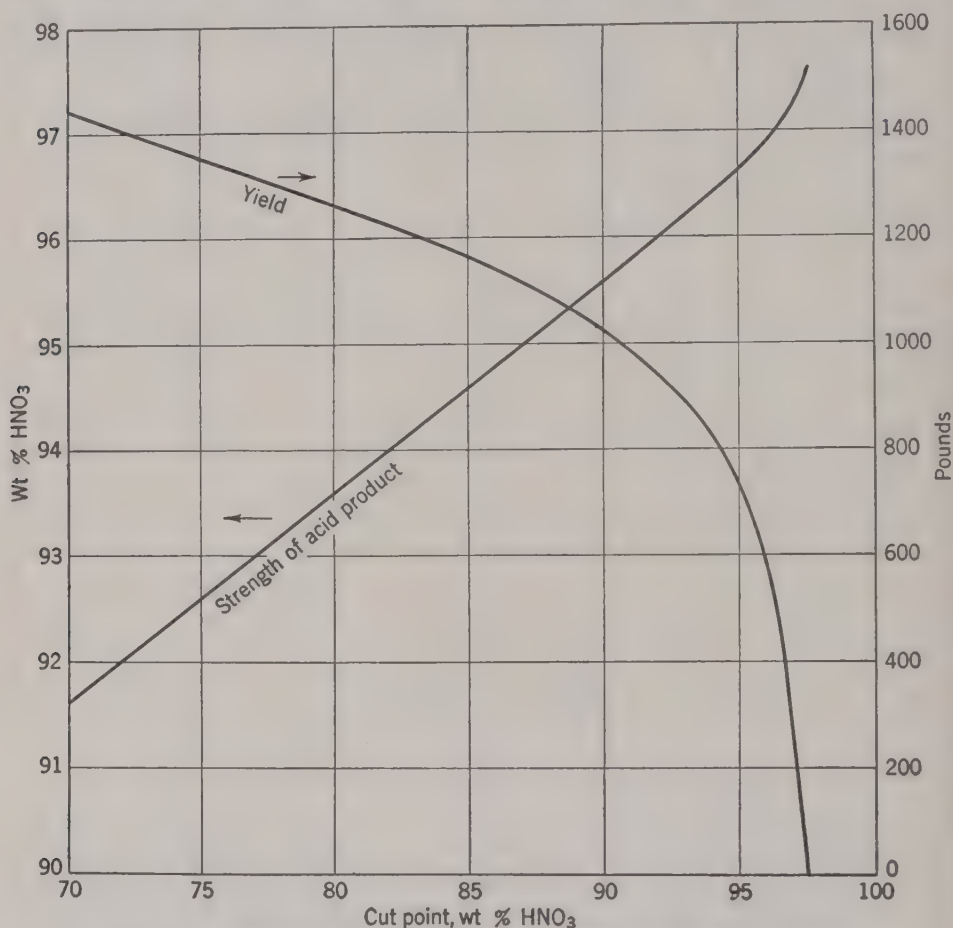


FIG. 7-5. Interrelation of cut point, strength of product, and yield.

cut is 95.6% HNO_3 . The results of a number of calculations of this sort are shown in Fig. 7-5, from which it can be seen that the proper "cut point" to use for production of 95% HNO_3 is 87%.

A report should take up the question of how to control the operation, point out that the initial and final cuts should be made at the same acid strength, and give the quantitative relations of cut point, strength of acid product, and yield, noting that the data on which these relations are based are self-consistent, within the usual limits of accuracy of plant measurements.

PROBLEMS

1. In a Haber plant the gas leaving the CuCl tower contains 75.16% H_2 , 24.57% N_2 , and 0.27% A. The gas entering the first bank of converters contains 79.52% H_2 , while the gas leaving the absorber, which follows the first bank, contains 80.01% H_2 . Absorption of NH_3 is substantially complete, and the design of the absorber is such that the amount of permanent gases removed from the system in the absorbing medium is negligible. What is the efficiency of utilization of H_2 in the first bank? What is the per cent conversion of H_2 per pass, *i.e.*, the mols of H_2 reacting to form NH_3 per 100 mols of H_2 entering the converters?

2. A synthetic-ammonia unit with a single converter is converting a fresh feed gas containing 75.8% H_2 , 23.7% N_2 , and 0.5% inerts. The gas leaves the converter containing 18.6% NH_3 and 70.0% H_2 . This converted gas is fed to a cooler under conditions of temperature and pressure such that most of the ammonia leaving the converter is condensed to a liquid and removed. On reduction of pressure all the dissolved gases are evolved from this liquid ammonia. These are compressed and returned to the system just before the cooler. The residual gases from the cooler are recycled to the inlet of the converter, except for a purge provided in the recycle line. The uncondensed ammonia leaving the cooler in these gases is found to be 8% of that leaving the converter. Calculate the amount and composition of the purged gases per 100 mols of feed gas, and determine the net mols of residual gas recycled to the converter inlet per 100 mols of feed gas.

3. Referring to the plant operations described in Illustration 1, calculate the following:

(a) The gas-recycle ratio for each of the last two banks, *i.e.*, the ratio of the total mols of gas recycled to the converters of the bank to the mols of gas fed to the bank from its preceding bank.

(b) The ratio of the total mols of gas entering each converter of each bank of the system to the fresh feed of purified gas entering the first bank.

(c) The percentage of the total ammonia synthesized in the whole system that is withdrawn from the system as pure liquid ammonia from the condenser unit of bank 2.

4. The proposal has been made to substitute for the condensation units of Illustration 1 a set of water absorbers to take up the ammonia, followed by driers to dehydrate the gas leaving the absorbers. Grant that one can thus remove the ammonia substantially completely from the gases and that the plant will adjust to the new situation by reducing the recycle ratio in each bank, with no other changes in operating conditions and without sacrifice of yield in any bank in the system. By what percentage will the recycle ratio in bank 1 be reduced?

5. Assuming that it is practicable to install a second converter in bank 3 of the plant of Illustration 1, the new converter to be operated in parallel with the present single converter of that bank and with the amount of recycle in this third bank increased so as to hold the total mols of gas entering each of the two converters at the same value as that now entering the single converter, but with no changes in the operation of the system, prior to the third bank, estimate the total percentage conversion of hydrogen plus nitrogen in the original fresh feed now obtainable in the system as modified.

6. In Illustration 3 accept the measured ammonia feed rate as a dependable figure, but in view of the uncertainty in the measured value of the rate of supply of primary air, treat this quantity as an unknown. Set up the three element balances around the whole of that part of the system prior to the absorption tower, and on the basis of these balances calculate the flow rates of primary air, drip acid, and nitrogen gas

in the gases entering the absorption tower. Compare the calculated air-flow rate with the reported measured value. On the basis of these results calculate the efficiency of conversion of ammonia to nitrogen oxides. *Ans.* 112%.

7. The burners of an ammonia oxidation unit at Billingham, England, are supplied with 1860 cu m/hr of NH_3 and 13,900 cu m/hr of primary air, measured at 0°C and 1 atm abs.* The ammonia feed amounts to 0.296 ton of ammonia per ton of equivalent 100% HNO_3 in the plant product. The burner gases pass to a cooling system in which the temperature of the gas stream is reduced to 30°C . The condensate formed as a result of this cooling contains approximately 30% HNO_3 . Both the condensate and the uncondensed gases flow to an oxidation and absorption system. To this system are fed 6600 cu m/hr of secondary air, measured at 0°C and 1 atm abs, and 178 gal of water per ton of equivalent 100% HNO_3 in the plant product. The liquid stream withdrawn from the oxidation and absorption system is a practically pure solution of HNO_3 in water, essentially free of lower oxides of nitrogen, and constitutes the main product of the plant. The gas stream leaving the oxidation and absorption system flows to an alkaline-absorption system. The absorbing medium supplied to the alkaline-absorption system is a 25% solution of NaOH , containing 0.040 ton of NaOH per ton of equivalent 100% HNO_3 in the plant product. The liquid withdrawn from the alkaline-absorption system is a neutral solution of NaNO_2 . The gases leaving the alkaline-absorption system pass through a back-pressure regulating valve, which maintains a pressure of 1.2 atm abs in the unit, and are then vented to the atmosphere. The plant production is 4.46 tons of equivalent 100% HNO_3 per hour.

(a) Compute the plant production in tons of equivalent 100% HNO_3 per hour from the reported ammonia feed rate and ratio of ammonia feed to plant product, and compare the result with the reported plant production.

(b) Compute the following quantities on the assumption that the reported plant production of 4.46 tons/hr corresponds to the HNO_3 in the main plant product (the liquid withdrawn from the oxidation and absorption system), while the reported figures for ammonia, water, and NaOH per ton of product are based on 1 ton of total product, *i.e.*, the nitrogen in the main product plus that in the nitrite liquor, expressed as 100% HNO_3 :

(1) Gallons per hour of water fed to the oxidation and absorption system. Compare the result with the value of 790 gal/hr given in the original report.

(2) Per cent HNO_3 in the liquid withdrawn from the oxidation and absorption system. Compare the result with the nominal strength of 50% HNO_3 given in the original report.

(3) Over-all recovery of nitrogen in the form of nitrate or nitrite, expressed as a percentage of the nitrogen in the ammonia feed.

(4) Per cent of total nitrogen recovered appearing in the nitrite liquor. Compare the result with the statement in the original report that from 5 to 10% of the nitrogen oxides are recovered in the nitrite liquor.

(5) Atoms per hour of nitrogen in the nitrite liquor and mols per hour of NaOH supplied to the alkaline-absorption system. Compare the result with the statement in the original report that the nitrite liquor is neutral.

(c) Repeat the calculations of part (b), assuming that the reported figure for the ammonia feed per ton of product is based on the total product, but that the reported figures for the water and NaOH per ton of product are based on the main product.

(d) Repeat the calculations of part (b), assuming that the reported figure for the ammonia per ton of product is based on the total product, the reported figure for the water per ton of product is the actual water rate in gallons per hour divided by 4.46,

* G. C. Inskeep and T. H. Henry, *Ind. Eng. Chem.*, **45**, 1386 (1953).

and the reported figure for the rate of supply of NaOH is the actual rate in tons per hour divided by 4.46. Assume, however, that the value of 4.46 is not the number of tons of HNO_3 in the main product and that in actual fact the main product contains 4.96 tons per hour of 100% HNO_3 .

(e) Granting that the efficiency of conversion of the nitrogen in the NH_3 to fixed nitrogen by the burner is 92.0%, estimate the atoms of fixed N and of active O per 100 mols of N_2 in the gas entering the oxidation and absorption system. How do you explain qualitatively the difference between the analyses of the gas and acid streams entering the oxidation and absorption system in the Billingham plant and the analyses of the corresponding streams entering the absorption column of the plant of Illustration 3?

8. A nitric acid plant uses carefully dried NaNO_3 of high purity and 98% H_2SO_4 containing an amount of H_2SO_4 that is 2% in excess of that theoretically required to convert the nitrate to NaHSO_4 . The amount of each of these materials to be introduced into the still for each batch is determined by careful weighing. In this plant the red acid produced from each batch is returned to the still with the charge for the next batch. The plant product is 96% acid of high purity, and the yield averages 98% of the theoretical for the nitrate used. The red acid produced from each batch averages 40 lb per 100 lb plant product. A representative sample of the red acid is taken, and 1 gram of this sample is diluted with 80% H_2SO_4 to 20 ml. Of this solution, 4 ml is tested in a nitrometer and yields 46 ml of NO, measured at normal barometer and 20°C. Another 10 ml of the same solution consumes 4.35 ml of $N/20$ KMnO_4 . Calculate the following quantities:

(a) Atoms of total nitrogen recovered and recycled in the red acid per 100 lb of product.

(b) Atoms of nitrogen as NO_2 and as HNO_3 in the red acid per 100 lb of product, calculated on the assumption that the nitrogen in the red acid is present only as NO_2 and HNO_3 .

(c) Pounds of water fed to the absorbers per 100 lb of product.

(d) Mols of total H_2O per mol H_2SO_4 that in your opinion should be fed to the still in the charge of mixed acids entering it.

(e) Pounds of 98% acid that should be weighed to accompany a 5000-lb charge of nitrate.

Chapter 8

LIME AND CEMENT

In lime burning the fuel consumption is often expressed as the "fuel ratio," *i.e.*, the pounds of lime produced per pound of fuel used. The fuel ratio can easily be estimated from the analysis of the kiln gas, provided the compositions of fuel and limestone are known.

Illustration 1. Consider the burning of pure calcium carbonate with hydrogen-free coke containing 83% carbon, producing a gas of the composition 26.5% CO₂, 5.0% O₂, and 68.5% N₂. It is required to compute the ratio of lime produced to coke burnt, the per cent excess air used in combustion, and the amount of stack gas per ton of lime.

Solution. This problem differs from one in simple combustion in that the gas contains not only the products of combustion of the fuel but also a reaction product from the charge, *i.e.*, the CO₂ from the limestone. In calculation, this CO₂ must be separated from the rest of the CO₂ that is a product of combustion. Since the nitrogen present in the gas comes from the air used for combustion, it may be employed as the basis for an oxygen balance in the manner illustrated under combustion calculations to get the oxygen actually introduced for combustion of the fuel. The balance of the oxygen must come from the limestone as CO₂. The following computation should be self-explanatory.

Basis: 100 mols of dry kiln gas.

Component	Mols	Mols O ₂	Atoms C
CO ₂	26.5	26.5	26.5
O ₂	5.0	5.0	
N ₂	68.5		
Total.....	100.0	31.5	
O ₂ from air, 68.5(21/79).....		18.2	13.3
O ₂ from stone \approx CO ₂ from stone.....		13.3	
C from fuel \approx O ₂ for combustion.....		13.2	

Weight CaO produced, 13.3(56.1) = 745 lb

Weight coke burnt, 13.2(12)/0.83 = 191 lb

Fuel ratio, lb CaO/lb coke, 745/191 = 3.9

Per cent excess air, 100(5.0/13.2) = 37.9%

Mols kiln gas per ton CaO, 2,000(100/745) = 268

Illustration 2. Take as a more practical problem the burning of a limestone containing, on the dry basis, 42.5% CO_2 and no other volatile matter, using coal containing 81.0% C, 4.7% H, 0.5% S, 1.8% N, 4.6% O, and 7.4% ash, and producing a stack gas containing 24.4% CO_2 , 4.1% O_2 , and 71.5% N_2 . Compute as in the previous case the fuel ratio, the excess air, and the stack gas per ton of lime.

Solution. Since the coal contains hydrogen, all the oxygen consumed in burning the fuel will not be present in the dry gas and the previous method must be modified. Preliminary calculations on the coal analysis are necessary.

Basis: 100 lb coal.

Constituent	Pounds	Mols or atoms	O_2 required
C.....	81.0	6.75	6.75
H_2	4.7	2.33	
O_2	4.6	0.14	
Net H_2	2.05	1.03
Total (neglecting S).....	7.78

This table shows that, for every 6.75 atoms of C, 7.78 mols of atmospheric oxygen are required for complete combustion. Of the oxygen used, however, 1.03 mols will not appear in the kiln-gas analysis because it represents oxygen combining with net hydrogen to form water.

Now consider the gas. The calculations are conveniently summarized in the following table.

Basis: 100 mols dry gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	24.4	24.4	24.4
O_2	4.1	4.1
N_2	71.5		
Total.....	100.0	24.4	28.5
C from coal, $14.9(6.75/7.78)$		12.9	
C from limestone.....		11.5	
O_2 from air, $71.5(21/79)$			19.0
O_2 excess.....			4.1
O_2 required for combustion.....			14.9

Pounds lime, $11.5(44)(100 - 42.5)/42.5^*$	685
Pounds coal, $12.9(100)/6.75$	191
Pounds lime per pound of coal, $685/191$	3.59
Excess air, $100(4.1/14.9)$	27.5%
Mols H_2O from combustion, $14.9(2.33/7.78)$	4.46
Total stack gas, $100 + 4.46$	104.46
Mols gas per ton of lime, $2000(104.46/685)$	305

* The figure 44 is the molecular weight of CO_2 .

It will be noted that the oxygen from the air is first calculated from the nitrogen. Next, the excess oxygen is "earmarked" and set aside, leaving 14.9 mols as the oxygen required for theoretical combustion. The calculations on the fuel analysis have given the ratio of carbon in the fuel to oxygen required for theoretical combustion, which is 6.75:7.78, making it possible to "earmark" similarly the carbon from the fuel and to get the carbon from the stone by difference. Having identified the amounts of all constituents in the gas from each source, it is a simple matter to get the quantities desired, as is shown by the calculations below the table.

The preceding examples serve to indicate the general method of computation. The illustration that follows shows how the method is applied to gas-fired kilns.

Illustration 3. A gas producer supplies the fuel for several lime kilns. Although the composition of the gas varies, the average of a number of analyses gives 9.5% CO_2 , 20.1% CO , 11.3% H_2 , 2.8% CH_4 , and 56.3% N_2 . Samples of the gas discharged by the kiln give 27.75% CO_2 , 2.25% O_2 , and 70.0% N_2 . Find, per pound of carbon burnt, the number of pounds of lime produced from a limestone of the composition 1.54% insoluble, 1.44% R_2O_3 (small iron), 50.07% CaO , and 3.54% MgO .

Solution. Examination of the kiln-gas analysis shows that its carbon comes from the producer gas and the limestone, its oxygen from three sources, fuel, limestone, and air, and its nitrogen from both air and fuel. Furthermore, the hydrogen in the fuel does not appear in the dry kiln gas. While the selection of a basis for calculation is somewhat arbitrary, there being no single factor connecting one stream with the others, nevertheless, as in the preceding cases, it will be found convenient to choose the kiln gas as the basis of computation.

Basis: 100 mols of dry kiln gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	27.75	27.75	27.75
O_2	2.25	2.25
N_2	70.0		
Total... ..	100.0	27.75	30.00

Now, since the quantities of the other three streams yielding this kiln gas are not determinable directly, let

x = the mols of producer gas

y = the mols of air

z = the mols of CO_2 from the limestone

Next the data from the analysis of the fuel are tabulated.

Basis: 100 mols of dry producer gas.

Gas	Mols	Atoms C	Mols H ₂	Mols O ₂
CO ₂	9.5	9.5	9.5
CO.....	20.1	20.1	10.05
H ₂	11.3	11.3	
CH ₄	2.8	2.8	5.6	
N ₂	56.3			
Total.....	100.0	32.4	16.9	19.55

Three simultaneous equations can be written expressing C, O₂, and N₂ balances, each on a basis of 100 mols dry kiln gas.

$$\text{C balance: } 0.324x + z = 27.75$$

$$\text{O}_2 \text{ balance: } (0.1955 - 0.169/2)x + 0.21y + z = 30.00$$

$$\text{N}_2 \text{ balance: } 0.563x + 0.79y = 70.00$$

The term $(0.1955 - 0.169/2)x$ in the O₂ balance is the oxygen in the producer gas going into the dry kiln gas. It is obtained by subtracting from the total oxygen in the fuel the oxygen equivalent of the hydrogen in it, because $(0.169/2)x$ mols of oxygen will not show up in the dry kiln gas. These equations when solved give

$$x = 45.1 \text{ mols of producer gas}$$

$$y = 56.5 \text{ mols of air}$$

$$z = 13.13 \text{ mols of CO}_2 \text{ from the limestone}$$

Another solution to the problem, not algebraic, follows:

Basis: 100 mols producer gas. The oxygen required for theoretical combustion is $32.4 + 16.9/2 - 19.55 = 21.3$ mols, the corresponding amount of nitrogen being $21.3(79/21) = 80.2$ mols. Adding this to the nitrogen already present in the fuel gives 136.5 mols as the total nitrogen produced by theoretical combustion. Hence, the ratio of carbon from the fuel to total "theoretical" nitrogen is $32.4/136.5$.

Basis: 100 mols dry kiln gas. Turning attention again to the kiln gas, it is seen that this contains 2.25 mols of O₂, the presence of which is due to excess air. The corresponding "excess" nitrogen is

$$2.25(79/21) = 8.47 \text{ mols}$$

The remaining nitrogen, $70.00 - 8.47 = 61.53$ mols, may be designated as the necessary, or theoretical, nitrogen coming from the theoretical combustion of the fuel. Using the ratio of carbon in the fuel to the theoretical nitrogen calculated above, $32.4/136.5$, the actual amount of CO₂ from the fuel present in 100 mols of kiln gas must be

$$(32.4/136.5)61.53 = 14.62 \text{ mols}$$

The remainder, $27.75 - 14.62 = 13.13$ mols, comes from the limestone. To calculate the amount of producer gas used, it will be noted that it must be sufficient to give 14.62 mols CO_2 . Since 100 mols of producer gas will yield 32.4 mols of CO_2 , $(100/32.4)14.62 = 45.1$ mols of producer gas will be necessary.

This solution involves earmarking and setting aside the nitrogen equivalent to excess air, the remaining nitrogen being that corresponding to theoretical combustion. Since the analysis of the fuel gives the ratio of the carbon in the fuel to the nitrogen for theoretical combustion, it is now possible to earmark the carbon from the fuel and get that from the stone by difference. This procedure illustrates the fact that earmarking frequently makes it possible to simplify computations by using arithmetic methods rather than algebraic. Algebraic methods, however, though sometimes more cumbersome, are more generally applicable.

The calculations by either method show that 45.1 mols of producer gas are required for each 13.13 mols of CO_2 produced from the stone, both on the basis of 100 mols of dry kiln gas. The producer gas is equivalent to $45.1(32.4/100)(12) = 175.5$ lb of carbon consumed in the producer. If the per cent of carbon in the coal is known, this figure can be converted into the corresponding weight of the coal.

In order to calculate the pounds of lime produced per pound of carbon consumed, the only remaining quantity to be determined is the pounds of lime produced, which is obtained through the analysis of the limestone.

Basis: 100 lb limestone.

	<i>Pounds nonvolatile</i>
Insoluble.....	1.54
R_2O_3	1.44
CaO	50.07
MgO	3.54
Total nonvolatile.....	56.59
CO_2 by difference.....	43.41
Mols CO_2 , $43.41/44$	0.985

The figure 43.41, obtained by difference from 100 of the sum of the other constituents, may be checked against the CO_2 corresponding to the CaO and MgO present. Theoretically, the CO_2 should be

$$50.07(44/56.1) + 3.54(44/40.3) = 43.15\%$$

The useful datum obtained from this analysis is the ratio, pounds of lime (nonvolatile material)/mols of CO_2 , which is 56.59:0.985.

Returning to the basis of 100 mols of kiln gas, 13.13 mols of CO_2 from the limestone are equivalent to $(56.59/0.985)13.13 = 755$ lb of lime.

The ratio, pounds of lime/pounds of carbon burnt in the producers, is $755/175.5 = 4.3$.

Illustration 4. An externally fired shaft lime kiln uses a coal of 14,160 Btu/lb as fired, which contains 78.31% C, 5.26% H, 1.55% N, 0.90% S, 6.37% ash, and 7.61% O. The kiln burns a limestone of high purity, producing on the average 2000 lb/hr of burnt lime. The average stack-gas analysis is 19.1% CO₂, 6.8% O₂, and 74.1% N₂. These gases leave the kiln at 300°C, and the lime is discharged at 250°C, air temperature being 20°C.

The heat of formation of CaCO₃ from CaO and CO₂ at 20°C is 43,700 cal/g mol. The average specific heat of CaO between 20°C and 250°C may be taken as 0.20.

Compute the following:

1. Fuel ratio, *i.e.*, the pounds of lime per pound of coal
2. Excess air used for combustion
3. Heat distribution in the kiln based on the lower heating value of the fuel

Solution. In order to get the coal and gas analyses into more useful form, they are recalculated as follows:

Basis: 100 lb of coal.

	Pounds	Mols or atoms	O ₂ required	H ₂ O
C.....	78.31	6.52	6.52	2.61
H ₂	5.26	2.61	
S.....	0.90	0.03	0.04	
O ₂	7.61	0.24		
Net H ₂ , 2.61 - 0.48.....	2.13	1.07	
Total.....	7.63	

Sulfur is converted to SO₃ in this kiln, being absorbed by the lime as CaSO₄.

Basis: 100 mols of stack gas.

Gas	Mols	Atoms C	Mols O ₂
CO ₂	19.1	19.1	19.1
O ₂	6.8	6.8
N ₂	74.1		
Total.....	100.0	19.1	25.9

From this table the following are computed by the techniques explained above:

O ₂ in entering air, 74.1(21/79).....	19.7
O ₂ in excess.....	6.8
O ₂ required for complete combustion.....	12.9
Total C present.....	19.1
C from coal, 12.9(6.52/7.63).....	11.0
C from stone.....	8.1
Lime produced, 8.1(56.1).....	454 lb*
Coal used, 11.0(100/6.52).....	169 lb
Pounds lime per pound coal, 454/169.....	2.68
Per cent of excess air, 100(6.8/12.9).....	52.7%
Mols H ₂ O from combustion, 2.61(12.9/7.63).....	4.4 mols
Mols gas passing through shaft per pound of lime produced, 104.4/454...	0.23 mol

On an hourly basis:

Lime produced.....	2000 lb
Coal used, 2,000(169/454).....	745 lb
Stone charged, 2000(100/56).....	3570 lb
Gas made, 2000(0.23).....	460 mols

These results are shown on Fig. 8-1.

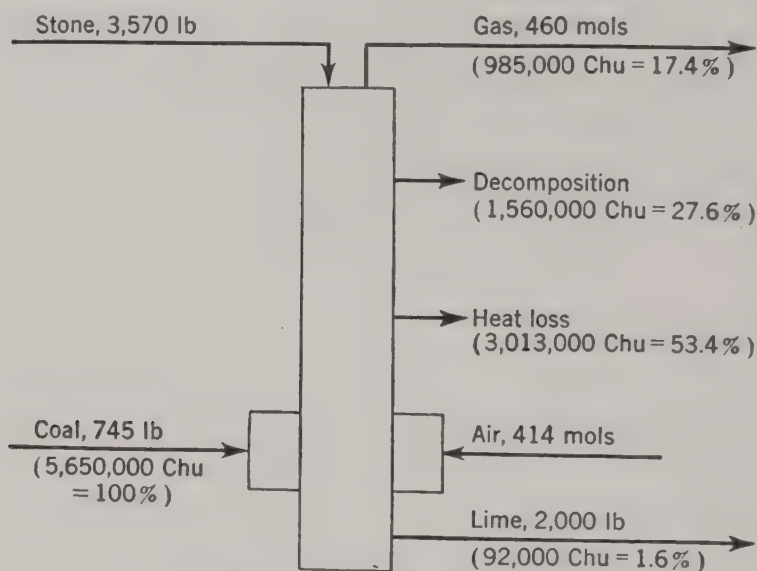


FIG. 8-1. Lime kiln. Basis: 1 hr.

In computing the heat distribution, it will be convenient to perform the calculations in Chu rather than in Btu since all temperatures are given in centigrade degrees. The heat of combustion of the coal is $14,160/1.8 = 7870$ Chu/lb, which is the higher heating value. This should be decreased by the amount necessary to vaporize the water

* Exclusive of the SO₃ absorbed, $0.03(12.9/7.63)80 = 4$ lb.

formed on combustion. Using 10,500 Chu per mol as the heat of vaporization gives $7870 - 10,500(2.61/100) = 7595$ Chu for the lower heating value. Thus, the heat input is $745(7595) = 5,650,000$ Chu/hr.

The heat output is made up of the sensible heat in the stack gas, the sensible heat in the hot lime, the heat of decomposition, and the radiation loss.

The sensible-heat content above 20°C of 100 mols of dry gas plus 4.4 mols of water vapor at 300°C is found by using Fig. 1-3 (page 15).

Basis: 100 mols of dry stack gas.

Gas	Mols	$Mc_{p,av}^{\circ}$ at $300^{\circ}\text{C} = 572^{\circ}\text{F}$	Mols $\times Mc_{p,av}^{\circ} \times 280$
CO_2	19.1	10.1	54,000
N_2	74.1	7.0	145,200
O_2	6.8	7.3	13,900
H_2O	4.4	8.3	10,200
Total.....	104.4		223,300

This and the other items of heat output are calculated on an hourly basis in the following table.

Basis: 1 hr.

	Chu	Per cent
Stack-gas loss per hour: (223,300/454)2,000.....	985,000	17.4
(985,000/5,650,000)100.....	
Heat in lime: 2,000(0.20)(250 - 20).....	92,000	1.6
(92,000/5,650,000)100.....	
Heat of decomposition: (2,000/56.1)43,700.....	1,560,000	27.6
(1,560,000/5,650,000)100.....	
Total heat accounted for.....	2,637,000	46.6
Heat loss by radiation, by difference.....	3,013,000	53.4
Total heat output = heat input.....	5,650,000	100.0

This kiln has an excessive fuel consumption, due to an inordinately large radiation loss. It should be examined to determine the cause of this loss and the defect remedied if practicable.

Illustration 5. The following data were obtained from a test on a rotary cement kiln, 135 ft in length and 76 in. in outside diameter. The mix was fed from a storage bin through a cast-iron pipe set in the brick

stack chamber. This dropped the charge into the rear of the kiln, whence it passed down toward the fire end, the time in the kiln being about an hour and a quarter. The fuel was finely powdered coal, from 100 to 200 mesh, blown in by compressed air under 60 to 70 lb pressure. From the fire end of the kiln the clinker dropped into a cooler, a cylindrical steel shell lined with firebrick, similar to the kiln but smaller in size. The clinker was cooled by cold air entering at the lower end of the cooler, flowing countercurrent to the clinker and feeding from the upper end into the kiln, furnishing the main air supply.

The object of the test was to determine (1) the pounds of coal consumed and pounds of raw mix used per 100 lb of clinker produced, and (2) the heat distribution.

The only weight measurement that was practicable to be taken was that of the cement produced; this was corrected for the gypsum added in order to get the clinker. Although the coal was weighed automatically for the entire plant of 25 kilns, some of these were 8 ft and some 10 ft in diameter, with widely different production and fuel consumption, so that the amount of fuel used in the kiln in question could not be measured directly, but had to be calculated from other data obtained in the test.

It should be noted that the temperature of the flue gas is probably somewhat in error. This was measured by a thermocouple inserted in the gas, which radiated heat to the colder walls and therefore read lower than the true temperature of the gas.

OPERATING DATA

Duration of test.....	8 hr
Cement produced (clinker plus gypsum).....	41,260 lb
Gypsum added.....	1,280 lb
Clinker produced, net.....	39,980 lb

Temperatures:

Clinker falling from kiln.....	2424°F
Maximum kiln temperature.....	2767°F
Clinker leaving cooler.....	1100°F
Flue gases.....	1411°F
Entering air:	
Wet bulb.....	23.6°F
Dry bulb.....	27.6°F

Barometer.....	29.9 in.
Anemometer, point of air entrance to cooler.....	244 ft/min

Average flue-gas analysis:	<i>Per cent</i>
CO ₂	25.39
O ₂	0.89
CO.....	0.08
N ₂	73.64

Clinker analysis:	Per cent
CaO.....	63.42
MgO.....	3.28
Fe ₂ O ₃ , Al ₂ O ₃	11.42
SiO ₂	20.80
SO ₃	0.63

Raw-mix analysis:	
CO ₂	33.34
CaO.....	41.97
SiO ₂	13.00
Fe ₂ O ₃ , Al ₂ O ₃	7.00
MgO.....	2.50
Graphite.....	0.65
FeS ₂	0.56
H ₂ O.....	0.71

Coal analysis:	
C.....	64.59
H.....	5.07
S.....	1.76
N.....	1.71
O.....	5.97
Moisture.....	0.86
Ash.....	20.04
Heat of combustion, 12,160 Btu	

Solution. There are three streams of materials entering the kiln—air, coal, and raw mix—and two leaving it—clinker and stack gas. Thus the problem involves the relation of these five quantities. By a nitrogen balance, however, the air used is a direct function of the gas evolved, thus reducing the quantities to four. If one of these is made the basis of calculation, three are left as unknowns. Let the basis of calculation be 100 lb of clinker and the unknowns:

x = pounds of coal per 100 lb of clinker

y = pounds of raw mix per 100 lb of clinker

z = mols of dry stack gas per 100 lb of clinker

Assume that all the ash from the coal enters the clinker and neglect the difference in composition between the clinker and the burnt portion of the stack dust. It is true that alkalis concentrate in the stack dust because of volatilization; but, as will appear, the ratios of raw mix, coal, and stack gas to clinker are computed by balances involving elements other than the alkalis, and since the amount of dust is not large and the percentages of these other elements in it do not differ greatly from those in the clinker, the error due to dust is slight. It does, however, follow that the "100 lb of clinker" used as a basis is the sum of the clinker

actually discharged from the firing end of the kiln plus the corresponding amount of burnt clinker going up the stack as dust. Any unburnt raw mix going up the stack as part of the total dust does not appear in the computations or affect them in any way.

To determine the three unknowns, three equations are necessary. The first of these is an oxygen balance, the second a carbon balance, and the third an equation of input to output of nonvolatile oxides.

Before setting up the actual equations, the various analyses are reevaluated in order to arrive more readily at the proper figures to be used.

Basis: 100 mols of dry stack gas.

Gas	Mols	Atoms C	Mols O ₂
CO ₂	25.39	25.39	25.39
O ₂	0.89	0.89
CO.....	0.08	0.08	0.04
N ₂	73.64		
Total.....	100.00	25.47	26.32

Basis: 100 lb of clinker.

	<i>Pounds</i>
CaO.....	63.42
MgO.....	3.28
Fe ₂ O ₃ , Al ₂ O ₃	11.42
SiO ₂	20.80
Nonvolatile oxides.....	98.92
SO ₃	0.63

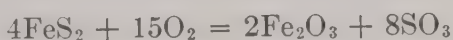
Basis: 100 lb raw mix.

	Pounds	Nonvolatile oxides	Atoms C
CO ₂	33.34	0.758
CaO.....	41.97	41.97	
SiO ₂	13.00	13.00	
Fe ₂ O ₃ , Al ₂ O ₃	7.00	7.00	
MgO.....	2.50	2.50	
Graphite.....	0.65	0.054
FeS ₂	0.56	0.37(Fe ₂ O ₃)	
H ₂ O.....	0.71		
Total.....	64.84	0.812

Basis: 100 lb coal.

	Pounds	Mols or atoms
C.....	64.59	5.38
H ₂	5.07	2.51
S.....	1.76	0.05
N.....	1.71	
O.....	5.97	0.37
Moisture.....	0.86	0.05
Ash.....	20.04	
Net H ₂ , 2.51 - 0.37.....	2.14

Although sulfur is present in both the coal and the raw mix, it is assumed that the stack gases contain none, since it is largely absorbed as sulfate by the lime and alkalis in the clinker and stack dust. The analysis of the clinker shows that over half the sulfur from the pyrites is converted to SO₃, and since the amount of FeS₂ present is small, little error will be introduced by assuming complete combustion to SO₃ by the reaction



Therefore, 15 mols of oxygen are required for every 4 mols of FeS₂. Likewise, the sulfur in the coal will be considered as oxidized to SO₃.

For the oxygen balance, the following equality must hold: (O₂ from air) + (O₂ from raw mix) = (O₂ in stack gas) + (O₂ for net H₂ in coal) + (O₂ for S in coal) + (O₂ for FeS₂ in raw mix). In this equation O₂ means only that oxygen that affects, or is affected by, the dry stack gas. Thus, combined water and moisture in the coal do not enter into account, nor does the oxygen in the form of the nonvolatile oxides, such as CaO, MgO, Al₂O₃, etc., come into consideration; yet the oxygen in the form of CO₂ in the carbonates in the raw mix must be allowed for, since it passes into the stack gases. Using the values obtained in the tabulated analyses and employing mols throughout, the oxygen balance becomes

$$0.7364z(21/79) + 0.00758y = 0.2632z + 0.0214x/2 + 0.0005x(3/2) + (0.0056/120)(15/4)y$$

Upon simplification this reduces to

$$0.00740y - 0.0115x = 0.0674z$$

Similarly, setting up the carbon balance

$$(\text{C from coal}) + (\text{C from raw mix}) = (\text{C in stack gas})$$

gives the following equation:

$$0.0538x + 0.00812y = 0.2547z$$

The equation for the nonvolatile oxides is

$$(\text{Oxides from raw mix}) + (\text{ash from coal}) = (\text{oxides in clinker})$$

giving

$$0.6484y + 0.2004x = 98.92$$

Solution of these three equations gives the following values:

$$x = 29.3 \text{ lb of coal}$$

$$y = 143.5 \text{ lb of raw mix}$$

$$z = 10.75 \text{ mols of stack gas}$$

These results may be used to determine the fuel consumption of the kiln. In the cement industry this is often expressed as *pounds of coal used* or as *Btu consumed* based on the higher heating value of the fuel *per barrel of cement*, a standard barrel being defined as 376 lb. In the present case this ratio equals $29.3(39,980)/(376)/100(41,260) = 107$ lb of coal per barrel. According to Dixon,¹ this figure is somewhat higher than usual for a kiln of the size in question. A study of the heat distribution ought to show where the major losses are occurring.

HEAT BALANCE

Normally, a heat balance is based upon the temperature of the surroundings, but in this case 60°F will be taken as a base line, partly for convenience (since Fig. 1-3 is based on this temperature) and partly to emphasize the fact that any reference point desired may be employed. Furthermore, although in furnace practice the heat balance is most frequently based on the higher heating value of the fuel as directly determined in a bomb or Junker's calorimeter (therefore including the heat of condensation of all water resulting from the combustion of the fuel), in this case the lower heating value will be employed. The use of the higher heating value is, in a very definite sense, illogical, because industrial furnaces are almost never in a position to recover this heat of vaporization of the water from the fuel, and hence to charge them with it in reporting their efficiency tends to give a distorted impression of their performance.

The heat balance will be that of the cooler and kiln combined. Here also the basis of calculation will be 100 lb of clinker.

¹ C. C. Furnas (ed.), "Rogers' Industrial Chemistry," 6th ed., Chap. 22, "Cement, Lime, and Plaster," by T. G. Dixon, D. Van Nostrand Company, Inc., New York, 1942.

Heat input. Heat of combustion of coal,

$$29.3(12,160) = 356,000 \text{ Btu}$$

Heat of vaporization of water formed on combustion,

$$29.3(0.0251 + 0.0005)(18)(1060) = 14,300 \text{ Btu}$$

The value 1060, taken from the steam tables, is the heat of vaporization of water at 60°F in Btu per pound. Net heat input from coal,

$$356,000 - 14,300 = 341,700 \text{ Btu}$$

Graphite has a heat of combustion of 94,100 Chu per atom of carbon, and the heat of combustion of FeS_2 , when burning to Fe_2O_3 and SO_3 , is 249,400 Chu per mol. The heat input due to the presence of these two substances in the raw mix is therefore

$$143.5[0.00054(94,100) + (0.0056/120)249,400]1.8 = 16,200 \text{ Btu}$$

Adding this to the 341,700 Btu already calculated gives 357,900 Btu as the total heat input.

Heat output.

1. *Heat of reaction.* In burning a raw mix to obtain cement, a number of chemical reactions take place. As the mix is heated, calcium and magnesium carbonates decompose into carbon dioxide and free lime and magnesia. The lime thus set free reacts with the silica, alumina, and iron oxide present in the mixture; free magnesia, apparently, has little tendency to combine. The over-all result is that, when the mixture has been heated to between 1400 and 1600°C and cooled, four definite compounds are predominant, namely, dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), and tetracalcium aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$). Microscopic studies have shown that in masses that are well mixed and well burnt the reactions are surprisingly complete. In fact, most cements contain about 1% or less of free lime, indicating that the rest has gone into the more complex compounds. Incompletely burnt clinkers are high in free lime and low in tricalcium silicate, indicating that the combination of free lime with dicalcium silicate is the last reaction to occur in the burning process.

To compute the heat of reaction for a complex operation of this sort obviously requires a more elaborate technique than has been employed in energy calculations up to this point. Fortunately, in the present case it is the over-all result that is of interest, and a consideration of the intermediate reactions is unnecessary.

The basic thermal data are available in a number of standard texts and collections of data¹ in the form of tables giving the heats of formation of various compounds from the elements of which they are composed. In applying the data to a chemical process, use is made of the principle developed in physical chemistry which states that, regardless of how many intermediate reactions are involved, the net heat effect is simply the difference between the heats of formation of the final products and the original reactants.

The data on heats of formation are in terms of chemical compounds; the analyses of the clinker and the raw mix, on the other hand, are largely in terms of oxides, without regard to the manner in which they are chemically combined. Clearly, the analyses must be expressed in terms of the chemical compounds actually existing in the clinker and the mix. To do this, a number of simplifying assumptions are necessary, since the analyses reported in this particular test are incomplete. These assumptions are justified by the fact that the uncertainties involve constituents that are present in minor amount. In addition, as will be shown, the over-all heat of reaction accounts for only about one-fifth of the total heat input to the kiln. Therefore, relatively large percentage errors in determining the heat of reaction have a relatively small effect on the over-all heat balance.

In estimating the composition of the clinker, the following items will be considered negligible:

1. Free CaO
2. Combined MgO
3. The amount of Fe_2O_3 in the clinker other than that derived from pyrites in the raw mix and the coal
4. Compounds of SO_3

All iron present in the clinker is considered to be present as tetracalcium aluminoferrite, the remaining alumina as tricalcium aluminate, and the remaining calcium combined with silica as dicalcium and tricalcium silicates.

Basis: 100 lb of clinker.

Pounds Fe_2O_3 : $143.5(0.0037) + 29,3(0.0176)(160)/32(4)$	1.18
Pounds Al_2O_3 : $11.42 - 1.18$	10.24
Total mols CaO: $63.42/56$	1.131
Total mols SiO_2 : $20.80/60.1$	0.346
Total mols Al_2O_3 : $10.24/102$	0.100
Mols MgO: $3.28/40.3$	0.081
Mols $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$: $1.18/160$	0.007
Mols $3\text{CaO}\cdot\text{Al}_2\text{O}_3$: $0.100 - 0.007$	0.093

¹ For example, J. H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., pp. 236-243, McGraw-Hill Book Company, Inc., New York, 1950; or F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, 1952.

Let x = the mols of dicalcium silicate and y the mols of tricalcium silicate. Then $x + y = 0.346$, while

$$2x + 3y = 1.131 - (4)(0.007) - (3)(0.093)$$

Solving,

$$x = 0.214 \text{ mols } 2\text{CaO}\cdot\text{SiO}_2$$

$$y = 0.132 \text{ mols } 3\text{CaO}\cdot\text{SiO}_2$$

The following assumptions are employed in estimating the composition of the raw mix:

1. All the MgO is in the form of MgCO_3
2. The rest of the carbonate is CaCO_3
3. Any CaO not present as carbonate is present as $\text{CaO}\cdot\text{SiO}_2$
4. The amount of Fe_2O_3 in the fraction reported as Fe_2O_3 and Al_2O_3 is negligible
5. Al_2O_3 is present as $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$

The computations that follow are on the same basis as above.

	<i>Mols</i>
Total CO_2 : $143.5(0.3334)/44$	1.088
MgCO_3 : $143.5(0.0250)/40.3$	0.089
CaCO_3 : $1.088 - 0.089$	0.999
Total CaO: $143.5(0.4197)/56$	1.076
$\text{CaO}\cdot\text{SiO}_2$: $1.076 - 0.999$	0.077
$\text{Al}_2\text{O}_3\cdot\text{SiO}_2$: $143.5(0.0700)/102$	0.099
Total SiO_2 : $143.5(0.1300)/60$	0.310
Free SiO_2 : $0.310 - 0.077 - 0.099$	0.134
Fe_2O_3 (from pyrites)*: $143.5(0.0037)/160$	0.003

* The heat of reaction associated with oxidation of FeS_2 in the mix to Fe_2O_3 and SO_3 has already been accounted for in the computation of the heat input to the kiln. The heat effects involved in further reactions of SO_3 are neglected here, as in the calculations concerning the clinker.

The approximate composition of the ash from combustion of the coal can be estimated if one knows the amounts of oxides present in it. The lime and silica can be found by taking the difference between the quantities in the raw mix and those in the clinker. The lime in the ash computed in this way is $1.131 - 1.076 = 0.055$ mol, or 3.08 lb. Similarly, the silica in the ash is $0.346 - 0.310 = 0.036$ mol, or 2.16 lb. Fe_2O_3 derived from oxidation of pyrites in the coal is computed directly and is $29.3(0.0176)(160)/(32)(4) = 0.65$ lb, giving a total of 5.89 lb of CaO, SiO_2 , and Fe_2O_3 in the ash. The total ash is $29.3(0.2204)$, which is also equal to 5.89 lb. The exact agreement between the two figures is fortuitous, but it justifies the assumption that the ash in this particular coal contains a negligible amount of Fe_2O_3 other than that derived from pyrites, as well as a negligible amount of MgO and Al_2O_3 . The assumption will be made that Fe_2O_3 is present in the ash as $\text{Fe}_2\text{O}_3\cdot\text{SiO}_2$, while

CaO and the remaining SiO_2 are combined partly as $\text{CaO} \cdot \text{SiO}_2$ and partly as $2\text{CaO} \cdot \text{SiO}_2$. Let u = the mols of $\text{CaO} \cdot \text{SiO}_2$ and v = the mols of $2\text{CaO} \cdot \text{SiO}_2$. Then $u + 2v = 0.055$ and $u + v = 0.036 - (0.65/160)$. Solving,

$$u = 0.009 \text{ mol } \text{CaO} \cdot \text{SiO}_2$$

$$v = 0.023 \text{ mol } 2\text{CaO} \cdot \text{SiO}_2$$

$$\text{Mols } \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 = 0.65/160 = 0.004$$

The calculated components of the raw mix, the ash from the coal, and the clinker are summarized in Table 8-1, together with the energy calculations.

TABLE 8-1. HEAT OF FORMATION OF CEMENT

Basis: 100 lb of clinker.

Compound	Mols	Heat of formation, Chu/lb mol *	Heat of formation, Chu	
			Reactants	Products
Raw mix plus ash:				
CaCO ₃	0.999	289,500	289,200	
MgCO ₃	0.089	261,700	23,300	
CaO·SiO ₂	0.077 + 0.009	377,900	32,500	
2CaO·SiO ₂	0.023	538,000	12,400	
Al ₂ O ₃ ·SiO ₂	0.099	642,000	63,600	
SiO ₂	0.134	203,350	27,200	
Fe ₂ O ₃	0.003	198,500	600	
Fe ₂ O ₃ ·SiO ₂	0.004	413,000	1,700	
Clinker:				
2CaO·SiO ₂	0.214	538,000	115,100
3CaO·SiO ₂	0.132	688,400	90,900
3CaO·Al ₂ O ₃	0.093	848,000	78,900
4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ ...	0.007	1,211,000	8,500
CaO.....	151,700	
MgO.....	0.081	143,840	11,600
Gas:				
CO ₂	0.999 + 0.089	94,052	102,200
Total.....	450,500	407,200

* Values for $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ from Rossini *et al.*, *op. cit.* Other values from Perry, *op. cit.* Value for $\text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$ estimated by adding the difference between the values for Fe_2O_3 and 2FeO to the value for $2\text{FeO} \cdot \text{SiO}_2$ from the first reference.

Therefore, the heat of reaction is $(450,500 - 407,200)1.8 = 78,000$ Btu.

2. *Sensible-heat content of gases.*

Basis: 100 mols dry stack gas.

Water vapor from air (pressure = 2 mm H₂O):

$$\frac{\text{Mols N}_2}{73.64} \left| \frac{\text{Mols air}}{100} \right| \frac{2}{758} = 0.246 \text{ mol H}_2\text{O}$$

Water vapor from charge:

$$\frac{\text{Mols gas}}{100} \left| \frac{\text{Lb charge}}{143.5} \right| \frac{\text{Lb H}_2\text{O}}{0.0071} \left| \frac{18}{10.75} \right| = 0.526 \text{ mol H}_2\text{O}$$

Water vapor from combustion of coal:

$$\frac{\text{Mols gas}}{100} \left| \frac{\text{Lb coal}}{29.3} \right| \frac{(2.51 + 0.05)}{10.75} = 6.99 \text{ mols H}_2\text{O}$$

Total water vapor:

$$0.246 + 0.526 + 6.99 = 7.76 \text{ mols}$$

SENSIBLE-HEAT CONTENT ABOVE 60°F

Gas	Mols	$Mc_{p,av}^\circ$ at 1411°F	Mols $\times Mc_{p,av}^\circ \times 1351$
CO ₂	25.39	11.4	392,000 Btu
O ₂	0.89	7.8	9,400
CO.....	0.08	7.4	800
N ₂	73.64	7.3	728,000
H ₂ O.....	7.76	8.9	93,500
Total.....	1,223,700 Btu

Basis: 100 lb clinker.

$$10.75(1,223,700/100) = 131,900 \text{ Btu}$$

3. Potential heat in gas due to CO.

$$10.75(0.0008)(67,600)(1.8) = 1050 \text{ Btu}$$

4. Sensible heat in clinker. Assume 0.25 as its average specific heat.

$$100(0.25)(1,100 - 60) = 26,000 \text{ Btu}$$

5. Heat required to bring charge, coal, and air to 60°F. Assume 0.20 as the specific heat of the solids and use 7.0 as the molal heat capacity of air.

					Btu
(143.5 + 29.3)(0.20)(60 - 27.6).....					1120
Mols gas	Mols N ₂	Mols dry air	Mols air	Btu/°F	
10.75	73.64	100	760	7.0	(60 - 27.6)..... 2280
	100	79	758		
Total.....					3400

6. Heat of vaporization at 60°F of water in charge.

$$143.5(0.0071)(1060) = 1080 \text{ Btu}$$

SUMMARY OF HEAT DISTRIBUTION

	Btu	Per cent
Heat input.....	357,900	100.0
Heat output:		
Heat of reaction.....	78,000	21.8
Sensible heat in gas.....	131,900	36.8
Potential heat in gas.....	1,050	0.3
Sensible heat in clinker.....	26,000	7.3
Heat required for charge.....	3,400	1.0
Heat to vaporize water in charge.....	1,080	0.3
Heat loss, by difference.....	116,470	32.5
Heat output = heat input.....	357,900	100.0

The summary of the heat calculations shows that the heat loss from the kiln is excessive, amounting to almost one-third of the heat input. The reason for this should be determined and the loss reduced if possible.

Another third of the heat input appears in the output as sensible heat in the stack gas. At first thought one might be inclined to suspect that this was caused by an unduly high amount of excess air. That this is not the case is quickly revealed by the gas analysis, which shows less than 1 per cent free oxygen. Little can be gained by reducing the per cent excess air, and other means of dealing with the stack losses should be investigated.

One possibility is to leave the conditions within the kiln itself unchanged and take steps to utilize the heat in the stack gases. For example, a waste-heat boiler might be installed. Another approach is to attempt to change the conditions inside the kiln in some way. To do this intelligently, it is necessary to understand the nature of these conditions and, in particular, to be aware of any equilibrium limitations that may exist. The final illustration of the chapter is concerned with this problem.

Illustration 6. Lacey and Shirley¹ give the data shown in Table 8-2 on the analysis of the solid charge at various distances from the discharge end of a 102-ft rotary cement kiln.

¹ W. N. Lacey and H. E. Shirley, *Ind. Eng. Chem.*, **24**, 332 (1932).

TABLE 8-2. ANALYSIS OF CHARGE IN CEMENT KILN

Distance from discharge end of kiln, ft	Weight per cent of sample		
	H ₂ O	CO ₂	Free CaO
102 (feed).....	1.4	31.2	0.9
87.....	0.4	30.1	1.2
66.....	0.2	25.9	6.6
54.....	0.1	22.9	11.7
42.....	0.1	14.9	19.6
33.5.....	0.2	8.9	26.1
29.....	0.2	5.9	26.3
24.5.....	0.1	2.6	28.2
18.....	5.0
14.....	4.2
10.....	2.7
7.....	0.3
4.....	0.2
0 (clinker).....	0.1

The feed contained 3.9% MgCO₃. Analysis of the clinker showed 64.3% CaO, 3.8% MgO, 23.1% SiO₂, 4.6% Al₂O₃, and 2.2% Fe₂O₃.

What do these data show about the operation of the kiln?

Discussion. Since the feed to this kiln contains only a small amount of MgCO₃, the percentage of CO₂ is an index primarily of the amount of undecomposed CaCO₃ in the charge. Inspecting the series of analyses with this in mind, one sees that there are five fairly distinct zones within the kiln. In the first zone, extending from the feed end to the sample point at 87 ft from the discharge end, there is only a small change in composition, indicating that little reaction of any kind is occurring. Essentially, the function of this part of the kiln is to dry and preheat the charge. In the second zone, from 87 ft to 33.5 ft, there is evident a progressive decrease in the percentage of carbonate and a simultaneous increase in free lime, indicating that the major reaction is decomposition of CaCO₃ to form CaO and CO₂. The third zone extends from 33.5 ft to 24.5 ft and is characterized by a continued decrease in carbonate, while the free lime remains practically constant. In this region there must be a disappearance of free lime through combination with other compounds in the charge at a rate approximately equal to that at which free lime is being formed by decomposition of CaCO₃. From 24.5 ft to 18 ft, the principal change is a sharp drop in the percentage of free lime, evidencing a high rate of reaction of free lime with other compounds. In the fifth and last zone, from 18 ft to the discharge end of the kiln, the residual free lime, which is still appreciable at 18 ft, is gradually eliminated.

While the broad outlines of the burning process are thus apparent, some kind of quantitative treatment of the data is obviously desirable. For

example, in any region in which the principal reaction is decomposition of CaCO_3 to form CaO and CO_2 , a comparison of the analyses ought to show that the increase in free CaO between any two points is stoichiometrically equivalent to the decrease in CaCO_3 between the same two points. If the data are compared properly, they can also be used to determine the relative rates of reaction in various parts of the kiln. Information on rates may well reveal features of the operation not immediately apparent from inspection of the tabulated analyses.

In view of the loss in weight resulting from evolution of H_2O and CO_2 as the charge moves through the kiln, the analyses as reported are not on the same basis. However, they are related by the fact that there is no change in the amounts of other oxides in the charge except for volatilization of negligible amounts of alkalis. Hence, the first step in the calculations is to express the analyses in terms of a fixed amount of nonvolatile oxides. At the same time, in order to make it easier to grasp the stoichiometrical relations, the carbon dioxide and the free lime should be expressed in terms of mols. For example, on a basis of 100 lb of nonvolatile oxides, the carbonate in the feed equals

$$31.2(100)/44(100 - 31.2 - 1.4) = 1.051 \text{ mols}$$

while the free lime equals $0.9(100)/56(100 - 31.2 - 1.4) = 0.024 \text{ mol}$. The results of similar calculations at other sample points are given in Table 8-3.

TABLE 8-3. CO_2 AND FREE CaO IN CEMENT-KILN CHARGE
Basis: 100 lb of nonvolatile oxides.

Distance from discharge end of kiln, ft	Mols CO_2	Mols free CaO
102.....	1.051	0.024
87.....	0.984	0.031
66.....	0.796	0.159
54.....	0.675	0.271
42.....	0.398	0.411
33.5.....	0.222	0.513
29.....	0.143	0.500
24.5.....	0.061	0.517
18.....	0.089
14.....	0.075
10.....	0.048
7.....	0.005
4.....	0.004
0.....	0.002

As has been noted previously, the amount of CO_2 in any given sample is an index chiefly of the content of CaCO_3 . However, the MgCO_3 in the feed amounts to several per cent and cannot be neglected. Some method of distinguishing between CO_2 evolved by decomposition of CaCO_3 and CO_2 from decomposition of MgCO_3 is needed.

The MgCO_3 in the charge may be present as such or in the form of dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$. However, both CaCO_3 and dolomite are relatively stable compounds, decomposing at about 890°C and 750°C , respectively, at normal atmospheric pressure, while MgCO_3 decomposes at a much lower temperature, approximately 540°C . Since the data indicate that some evolution of CO_2 takes place even in the first 15 ft of travel of the charge through the kiln, where the temperature of the charge is still quite low, it seems likely that MgCO_3 is decomposing in this zone before the charge is heated sufficiently to effect any appreciable decomposition of CaCO_3 or of dolomite and, therefore, that MgCO_3 is present as magnesium carbonate and not as dolomite.

This conclusion is also reached by another line of reasoning. The evolution of CO_2 is $1.051 - 0.984 = 0.067$ mol in the first zone of the kiln, while the gain in free CaO is only $0.031 - 0.024 = 0.007$ mol. Conceivably, this result might be attributed to the decomposition of 0.067 mol of CaCO_3 , followed by reaction of 0.060 mol of free CaO with other solid oxides in the charge. However, the rate of reaction of free CaO with solid oxides does not become equal to the rate of decomposition of CaCO_3 until a point somewhere in the middle of the kiln is reached where the temperatures are much higher. This further strengthens the likelihood that the early CO_2 evolution is from magnesium carbonate. It is more reasonable, therefore, to assume that only 0.007 mol of CaCO_3 decomposes in the first zone and that the decomposition of MgCO_3 amounts to 0.060 mol. It will further be assumed that any undecomposed MgCO_3 remaining at the 87-ft mark is decomposed in the interval between 87 and 66 ft. Since the MgCO_3 is a minor constituent, the effect of any error in these assumptions on a study of the major reactions occurring in the kiln should be small.

The MgCO_3 in the feed equals

$$3.9(100)/(100 - 31.2 - 1.4)(84) = 0.069 \text{ mol}$$

By difference, the CaCO_3 in the feed equals $1.051 - 0.069 = 0.982$ mol, and the CaCO_3 at the 87-ft mark equals $0.982 - 0.007 = 0.975$ mol. Since 0.060 mol of MgCO_3 is decomposed between 102 and 87 ft and the remaining 0.009 mol between 87 and 66 ft, the mols of CO_2 at 66 ft and at succeeding sample points are numerically equal to the mols of CaCO_3 .

Table 8-4 presents the data recomputed in terms of MgCO_3 , CaCO_3 , and free CaO .

TABLE 8-4. CARBONATES AND FREE CaO IN CEMENT-KILN CHARGE
Basis: 100 lb of nonvolatile oxides.

Distance from discharge end of kiln, ft	Mols MgCO ₃	Mols CaCO ₃	Mols free CaO
102.....	0.069	0.982	0.024
87.....	0.009	0.975	0.031
66.....	0.000	0.796	0.159
54.....	0.675	0.271
42.....	0.398	0.411
33.5.....	0.222	0.513
29.....	0.143	0.500
24.5.....	0.061	0.517
18.....	0.089
14.....	0.075
10.....	0.048
7.....	0.005
4.....	0.004
0.....	0.002

With the data in this form a study of the two major reactions, decomposition of calcium carbonate and reaction of free lime with the other oxides, can now be made.

As an aid to visualization, the data of columns 1 and 3 of Table 8-4 are plotted as the solid line in Fig. 8-2. The curve shows in a general way that the amount of undecomposed CaCO₃ in the solid charge drops off at a fairly constant rate in the region between 87 and 18 ft. This means that decomposition of CaCO₃ is a relatively slow reaction, requiring almost three-quarters of the entire length of the kiln for completion.

A more severe test of the data is to consider the average rate of decomposition within the intervals between sampling points. *If all other conditions were equal*, the number of mols of CaCO₃ decomposed within any given section of the kiln should be proportional to the average number of mols of undecomposed CaCO₃ present in the charge as it passes through the section. The number of mols decomposed is also undoubtedly proportional to the residence time of the charge within the section; and the residence time, in turn, is probably roughly proportional to the length of the section. Therefore, *if all other conditions were equal*, the ratio of the number of mols of CaCO₃ decomposed to the product of the length of the section and the average number of mols of CaCO₃ present should be nearly constant. The actual values of the ratio serve to indicate how conditions affecting the rate of decomposition of CaCO₃ vary within the kiln.

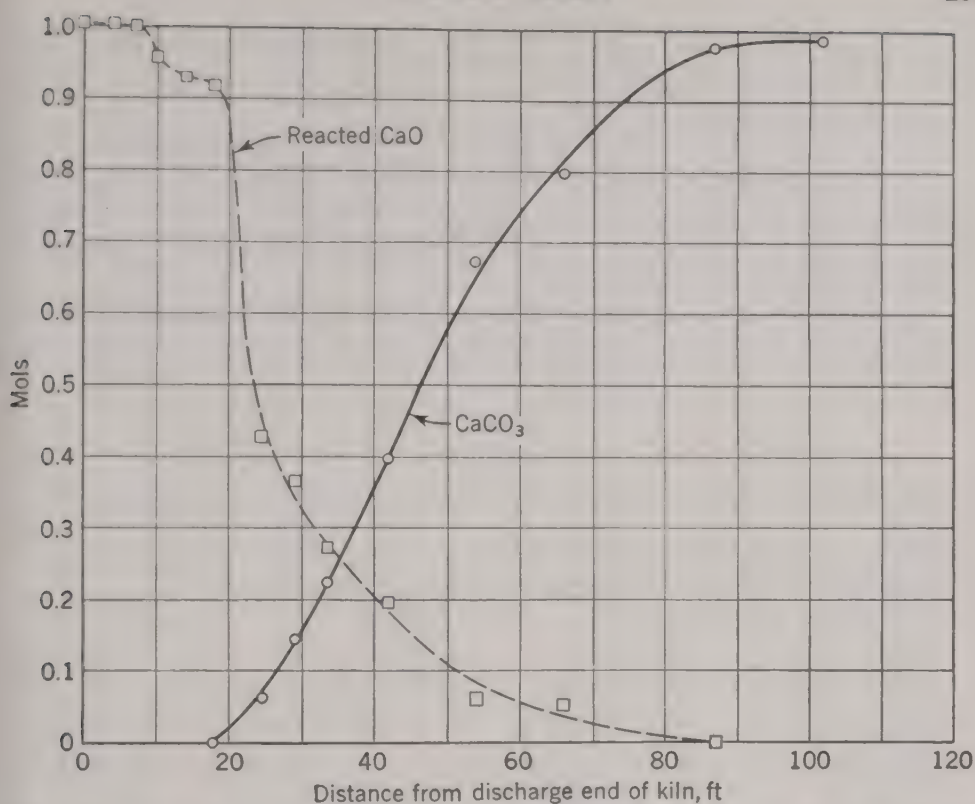


FIG. 8-2. Analyses of the solid charge in the cement kiln of Illustration 6. Basis: 100 lb of nonvolatile oxides.

TABLE 8-5. RATE OF DECOMPOSITION OF CaCO_3

Basis: 100 lb of nonvolatile oxides.

Distance from discharge end of kiln, ft	Length of interval, ft	Av distance from discharge end of kiln, ft	Av mols of CaCO_3 present	Mols of CaCO_3 decomposed	Mols of CaCO_3 decomposed per foot per mol of CaCO_3 present
102 — 87	15	94.5	0.979	0.007	0.0005
87 — 66	21	76.5	0.886	0.179	0.0096
66 — 54	12	60	0.736	0.121	0.0137
54 — 42	12	48	0.537	0.277	0.0429
42 — 33.5	8.5	37.75	0.310	0.176	0.0667
33.5 — 29	4.5	31.25	0.183	0.079	0.0957
29 — 24.5	4.5	26.75	0.102	0.082	0.179
24.5 — 18	6.5	21.25	0.031	0.061	0.302

Values of the desired ratio are easily computed from the data of Table 8-4; the calculations are summarized in Table 8-5 and the results shown graphically in Fig. 8-3.

Because a plot based on differences is inherently a more severe test of the accuracy of the original analyses than is a plot of the total number of mols, the fact that the points on Fig. 8-3 fall on a relatively smooth curve is a strong confirmation of the general dependability of the techniques of sampling and analysis employed by Lacey and Shirley.

As might be expected, Fig. 8-3 shows that the rate of decomposition of CaCO_3 is very low in the early stages, being almost negligible from

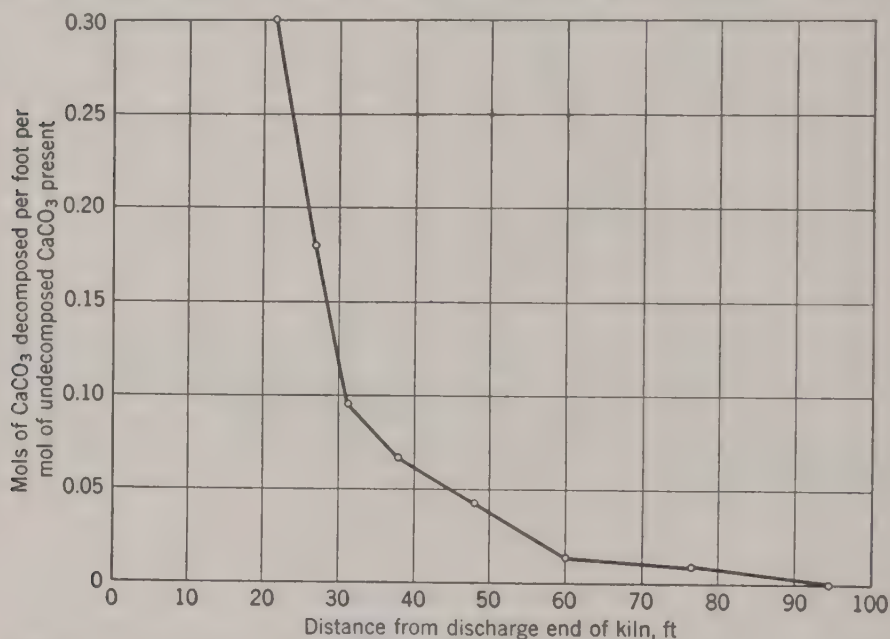


FIG. 8-3. Rate of decomposition of CaCO_3 in the cement kiln of Illustration 6.

the entrance end of the kiln to a point about 60 ft from the discharge end, and then rises progressively until the CaCO_3 completely disappears. The surprising aspect of the data is that the rate of decomposition increases no more than it does. Thus, from a value of about 0.014 at 60 ft the rate increases to about 0.30 at 21.25 ft, a twenty-one-fold increase. Remembering that the rates of many chemical reactions double with increase in temperature of the order of magnitude of only 10 centigrade degrees¹ (*i.e.*, exhibit a thirty-two-fold increase with a temperature rise of the order of only 50 centigrade degrees), one realizes that the increase in the rate of decomposition of CaCO_3 as the charge progresses through the kiln is indeed remarkably small. The full significance of

¹ This is an approximation for homogeneous reactions at ordinary temperatures. The effect of temperature on reaction rate is less at elevated temperatures.

this fact will become plainer after discussion of energy and temperature effects (see pages 275 and 276).

Another revealing test of the data is to compare the increase in CaO in each interval with the corresponding decrease in CaCO_3 . When decomposition of CaCO_3 is the only reaction, the molal ratio of these two quantities should equal 1. Actually, as may be seen from the last column shown in Table 8-6, the ratio has an average value of over 0.8 from the feed end of the kiln to the 54-ft point, *i.e.*, for a distance of 48 ft. To this point, then, only a relatively small fraction of the CaO produced by decomposition of CaCO_3 is being consumed by reaction with SiO_2 ,

TABLE 8-6. RATIO OF CaO ACCUMULATED TO CaCO_3 DECOMPOSED
Basis: 100 lb of nonvolatile oxides.

Distance from discharge end of kiln, ft	Mols of CaCO_3 decomposed	Mols of free CaO accumulated	Free CaO accumulated CaCO_3 decomposed
87 - 66.....	0.179	0.128	0.72
66 - 54.....	0.121	0.112	0.93
54 - 42.....	0.277	0.140	0.51
42 - 33.5.....	0.176	0.102	0.58
33.5 - 29.....	0.079	-0.013	-0.16
29 - 24.5.....	0.082	0.017	0.21
24.5 - 18.....	0.061	-0.428	-7.0

etc. However, in the range from 54 to 24.5 ft, the ratio drops off toward zero. For this fact the only possible explanation is that an ever-increasing proportion of the free CaO produced by decomposition of the carbonate is being consumed by reaction with SiO_2 , Fe_2O_3 , and with previously formed silicates of calcium and aluminum. The last value in the ratio column, being distinctly negative, must mean that here free CaO is reacting at a much faster rate than it is being produced from CaCO_3 . In short, the table discloses that the main reaction from 87 to 54 ft is $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$, and from 24.5 ft to the discharge end it is the disappearance of free CaO, while the distance from 54 to 24.5 ft is a transition region in which both reactions are important. This means that the boundary between the second and third zones in the kiln, originally judged to be at a distance of about 33.5 ft from the discharge end, is actually about 54 ft from the discharge end.

Since it is the combination of free lime with the other oxides that makes cement, a further study of this reaction is especially desirable. To follow its course, one needs a "tracer," a substance that can be used to indicate the progress of reaction despite the fact that another reaction, the

decomposition of CaCO_3 , is simultaneously going on in the transition zone described above. For this purpose the significant value is the difference between the sum of the mols of CaCO_3 and free CaO in the feed and the sum of the mols of CaCO_3 and free CaO at any given sample point. This difference, which may be called "reacted CaO ," is the amount of free CaO that has combined with other compounds between the feed end of the kiln and the sample point. For example, in the feed the CaO present as CaCO_3 and free CaO amounts to

$$0.982 + 0.024 = 1.006 \text{ mols}$$

At a distance of 29 ft from the discharge end, the CaO present as CaCO_3 and free CaO is $0.143 + 0.500 = 0.643$ mol. The difference, 0.363 mol, must be present at the 29-ft sample point in combination with SiO_2 , Al_2O_3 , etc. Values of "reacted CaO ," computed in this way, are given in Table 8-7 and appear as the dotted line in Fig. 8-2.

TABLE 8-7. REACTED CaO IN CEMENT-KILN CHARGE

Basis: 100 lb of nonvolatile oxides.

Distance from discharge end of kiln, ft	Mols of reacted CaO
102.....
87.....
66.....	0.051
54.....	0.060
42.....	0.197
33.5.....	0.271
29.....	0.363
24.5.....	0.428
18.....	0.917
14.....	0.931
10.....	0.958
7.....	1.001
4.....	1.002
0.....	1.004

Just as the mols of CaCO_3 decomposed per foot per mol of undecomposed CaCO_3 present is a good index of conditions affecting the rate of decomposition, so the mols of free CaO reacting per foot per mol of free CaO present can be taken as an index of conditions affecting the rate of combination of free CaO with other compounds in the charge. The computations are given in Table 8-8 and the results presented graphically in Fig. 8-4.

TABLE 8-8. RATE OF REACTION OF CaO IN CEMENT KILN

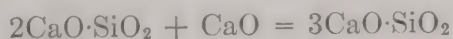
Basis: 100 lb of nonvolatile oxides.

Distance from discharge end of kiln, ft	Length of interval, ft	Av distance from discharge end of kiln, ft	Av mols of free CaO present	Mols of free CaO reacted within the interval	Mols of free CaO reacted per foot per mol of free CaO present
66 — 54	12	60	0.215	0.009	0.003
54 — 42	12	48	0.341	0.137	0.033
42 — 33.5	8.5	37.75	0.471	0.074	0.018
33.5 — 29	4.5	31.25	0.507	0.092	0.040
29 — 24.5	4.5	26.75	0.509	0.065	0.028
24.5 — 18	6.5	21.25	0.303	0.489	0.248
18 — 14	4	16	0.082	0.014	0.043
14 — 10	4	12	0.064	0.027	0.105
10 — 7	3	8.5	0.027	0.043	0.530
7 — 4	3	5.5	0.005	0.001	0.067
4 — 0	4	2	0.003	0.002	0.167

The values in the fourth column are calculated from the figures in Table 8-4 (page 268), while those in the fifth column are obtained by taking the differences between values for reacted CaO found in Table 8-7. The ratios in the last column come from division of the fifth column by the product of the second and fourth.

As with decomposition of CaCO_3 , here, too, a consideration of rates is most illuminating. Figure 8-4 shows that the reaction of free CaO with other constituents in the charge occurs in three distinct stages. In the third zone of the kiln, from 54 ft to 24.5 ft, reaction begins to take place but is fairly slow and amazingly constant. In the fourth zone, from 24.5 to 18 ft, the rate of reaction increases very rapidly within a short distance of travel along the kiln and then decreases with equal rapidity to an almost negligible value. In the fifth zone, the rate goes through another, larger "hump."

Evidently, the two "humps" in the curve of Fig. 8-4 must reflect the existence of two stages in the reaction of free CaO with other compounds in the charge. Mention has already been made of the fact that poorly burnt clinker contains free CaO and is lower in its content of $3\text{CaO}\cdot\text{SiO}_2$ than a well-burnt product. Hence, one might guess that the first stage involves formation of $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, while the second stage consists of the reaction



If this guess is right, the number of mols of CaO reacting in the fifth zone should be equal to the number of mols of $3\text{CaO}\cdot\text{SiO}_2$ in the clinker.

The required comparison is easily made and shows that the number of mols of CaO reacting in the fifth zone, $1.004 - 0.917$ mol, is only a little more than a third of the number of mols of $3\text{CaO}\cdot\text{SiO}_2$ in the clinker, calculated from the clinker analysis by the methods of Illustration 5. One is forced to conclude that the first stage involves not only the formation of $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, but also that of roughly two-thirds of the $3\text{CaO}\cdot\text{SiO}_2$ in the final product. Presumably the reaction $2\text{CaO}\cdot\text{SiO}_2 + \text{CaO} = 3\text{CaO}\cdot\text{SiO}_2$ is not completed in the first stage because of some kind of equilibrium limitation. This may be

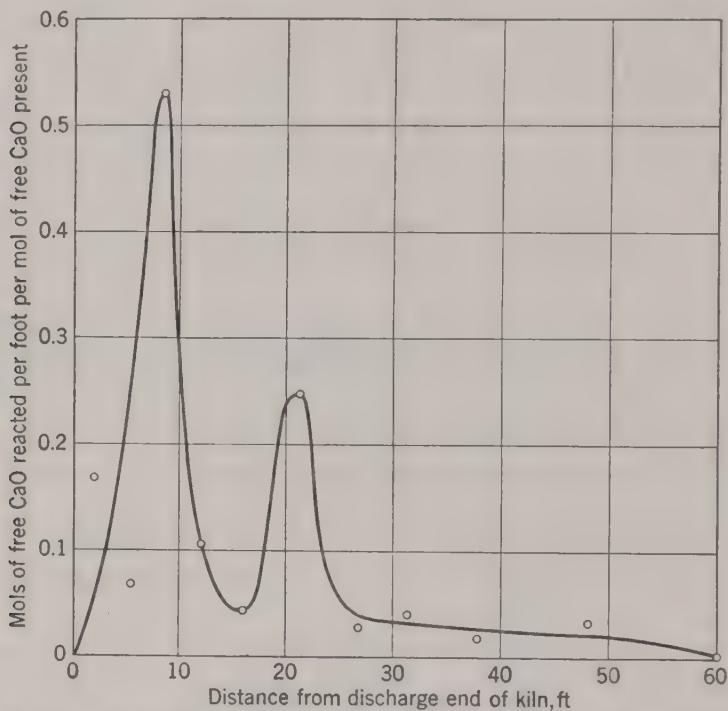


FIG. 8-4. Rate of reaction of free CaO in the cement kiln of Illustration 6.

a so-called "false equilibrium" or, indeed, a true chemical equilibrium. Whatever its nature, the limitation is progressively removed as the charge is subjected to ever higher temperatures in moving through the fifth zone.

HEAT OF REACTION

Analysis of the data has shown that conversion of the feed to cement is not a simple chemical reaction. Rather, it is the result of four stages, which overlap to some degree but are nevertheless fairly distinct. Consideration of the heat effect associated with each stage is worthwhile.

The stages to be considered are (1) decomposition of MgCO_3 , (2) decomposition of CaCO_3 , (3) reaction of free CaO with the charge to

produce an incompletely burnt clinker, and (4) completion of the reaction $\text{CaO} + 2\text{CaO} \cdot \text{SiO}_2 = 3\text{CaO} \cdot \text{SiO}_2$. The composition of the clinker and feed may be estimated by the methods of Illustration 5 and the heats of reaction computed with the aid of the heats of formation listed on page 262. The results appear in Table 8-9.

TABLE 8-9. HEAT OF REACTION OF CEMENT

Basis: 100 lb of nonvolatile oxides.

Stage	Reaction	Heat of reaction, Chu
1	$0.069 \text{ MgCO}_3 = 0.069 \text{ MgO} + 0.069 \text{ CO}_2$	- 1,650 (heat absorbed)
2	$0.982 \text{ CaCO}_3 = 0.982 \text{ CaO} + 0.982 \text{ CO}_2$	- 43,000 (heat absorbed)
3	$0.895 \text{ CaO} + 0.165 \text{ CaO} \cdot \text{SiO}_2 + 0.045 \text{ Al}_2\text{O}_3 \cdot \text{SiO}_2 + 0.014 \text{ Fe}_2\text{O}_3 + 0.175 \text{ SiO}_2$ $= 0.244 \text{ 2CaO} \cdot \text{SiO}_2 + 0.141 \text{ 3CaO} \cdot \text{SiO}_2$ $+ 0.031 \text{ 3CaO} \cdot \text{Al}_2\text{O}_3 + 0.014 \text{ 4CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	+ 5,900 (heat evolved)
4	$0.087 \text{ CaO} + 0.087 \text{ 2CaO} \cdot \text{SiO}_2 = 0.087 \text{ 3CaO} \cdot \text{SiO}_2$	+ 110 (heat evolved)
Over-all reaction, $44,650 - 6,010 = 38,640$ Chu absorbed $\approx 70,000$ Btu absorbed		

Inspection of the table shows that decomposition of CaCO_3 requires a large amount of heat, more than seven times as much as the heat effect of any other reaction in the kiln. An important question is that of the temperature level at which this heat must be supplied. As has already been noted, the dissociation pressure of CO_2 over CaCO_3^* is 1 atm at about 890°C . The partial pressure of CO_2 in the kiln gases is about 0.25 atm (see Illustration 5), which is the dissociation pressure of CaCO_3 at about 810°C . Since the dissociation pressure exceeds the partial pressure of CO_2 in the gases passing through the kiln at all temperatures above 810°C , it would appear that the CaCO_3 should decompose as soon as the temperature exceeds 810°C . However, as will be shown, the driving force due to the existence of this pressure differential is not enough to cause significant decomposition of CaCO_3 below 890°C .

A major barrier to decomposition at temperatures below 890°C is the fact that at any instant the bulk of the charge is located in a pool along the bottom of the kiln and is in a relatively quiescent state. Contact between the main stream of gas and the large pool of charge is poor, and there is relatively little tendency for CO_2 -rich gas in immediate contact with the solid in the pool to be transferred to the main stream of gas. Therefore, until the pressure of CO_2 exerted by CaCO_3 reaches atmos-

* The dissociation pressure of CO_2 over CaCO_3 , i.e., its equilibrium pressure over a mixture of CaCO_3 and CaO , is given in Fig. 10-3.

pheric pressure and the CaCO_3 begins to "boil," little decomposition of the solid in the pool occurs.

To be sure, at any instant there is a certain fraction of the charge that is in the process of dropping through the gas stream and is therefore in good contact with it. During its transit from the top to the bottom of the kiln, each particle is heated to a temperature that is probably well above that of the large pool into which it falls. However, as soon as a particle falls into the pool, the large heat capacity of the pool and the mixing effect due to rotation of the kiln act to bring the temperature of the particle down to that of the pool almost immediately. The net result is that at any time the fraction of particles in the kiln at temperatures above that of the pool is small and the time during which any individual particle is at a temperature well above that of the pool is short.

In spite of the brief time of exposure of any given particle to high temperature, significant decomposition might occur if the process of decomposition were extremely rapid. However, like many decomposing solids, CaCO_3 has a strong tendency to superheat, and laboratory experiments at atmospheric pressure have shown that particles of CaCO_3 may be heated to as much as 40 or 50 degrees above 890°C and still take from half an hour to an hour to decompose. One must conclude that decomposition of CaCO_3 is delayed until the charge as a whole is heated to a temperature sufficient to cause CaCO_3 to "boil." Because of superheating, this temperature will be somewhat above the equilibrium temperature of 890°C .

Since the heat required to decompose CaCO_3 must be supplied at a high temperature level, the temperature difference available as the driving force for transfer of this heat is comparatively small. Furthermore, the amount of heat that must be transferred is large. It therefore seems highly probable that the rate at which decomposition can occur is limited by the rate at which heat can be supplied to the surface of the CaCO_3 . This is the most likely explanation for the fact, already observed, that decomposition of CaCO_3 is a relatively slow reaction.

The large absorption of heat attendant upon decomposition of CaCO_3 also suggests an explanation for the fact that the rate of reaction of free CaO with the charge is comparatively low and constant as long as the charge contains an appreciable amount of decomposing CaCO_3 but increases rapidly as soon as the amount of CaCO_3 becomes small. Clearly, the presence of a considerable number of particles of CaCO_3 decomposing at a temperature in the neighborhood of 890°C and simultaneously absorbing large amounts of heat has a tendency to keep the rest of the charge at a temperature not much in excess of 890°C . Only when CaCO_3 has largely disappeared can the charge be heated to the

higher temperature range necessary for the formation of clinker at a high rate.

While the table shows that the heat effect associated with the third stage of reaction is comparatively small, the fact that it is exothermic means that it tends to kindle the reaction. Therefore, once the charge is raised to a temperature at which reaction begins to be rapid, the rate increases very rapidly indeed and the reaction is soon completed, in so far as is possible at the temperatures existing in this region of the kiln.

The heat of reaction of the fourth stage is so small that its effect on the progress of events is negligible.

HEAT EXCHANGE

As was pointed out in Chap. 3, the relationships between heat transferred and temperature level are often of great importance to the engineer. In the present case, in which a considerable amount of heat must be furnished at high temperature, a clear understanding of the relations is essential to intelligent control.

Unfortunately, heat exchange in the kiln is much more complex than in any of the cases treated in Chap. 3. To be sure, the charge is heated by combustion gases, which flow in a direction countercurrent to that of the charge, and the kiln may be looked upon as a countercurrent heat exchanger. However, no material was transferred between the hot and cold streams in the illustrations given in Chap. 3. In the cement kiln, on the other hand, there is a transfer of water, carbon dioxide, dust, and volatile alkalies. In Chap. 3, the assumption was made that the heat lost by the hot stream in any given section of the apparatus was equal to that gained by the cold stream in the same section. In the kiln, because of heat losses to the surroundings and radiation in a lengthwise direction, this assumption may be far from justified in some parts of the unit. In the problems of Chap. 3, both streams were fluids under conditions of turbulence such that one could assume each stream to be nearly uniform in temperature at any given cross section perpendicular to flow. In the kiln, the particles dropping through the gas are appreciably hotter than those in the pool at the bottom. Furthermore, there is a possibility that sharp temperature gradients may develop within a single particle.

When faced with a complex situation such as this, one can make use of a technique of great value in many areas of thought.¹ The first step is to imagine a simplified, idealized picture of whatever is being studied. The second step is to focus upon the differences between this picture and the actual situation. When this is done, one often finds that the deviations are relatively small. Furthermore, a study of the deviations

¹ Perhaps the most famous example is Plato's "Republic."

often reveals a pattern that can be described, sometimes qualitatively, sometimes quantitatively. The net result is that it becomes much easier to understand the whole complicated situation. Instead of being confused by a mass of details, one has to think of only two rather simple ideas, an idealized picture and a pattern of deviations.

As applied to the cement kiln of Illustration 6, the first step is to imagine that the charge is heated and the gases cooled by an idealized process, which is simplified enough to be analyzed by the methods of Chap. 3. The results can then be compared with Figs. 8-3 and 8-4 and some conclusions drawn as to the difference between the idealized process and the actual operation of the unit. Finally, in the light of all this, the whole performance of the kiln can be reviewed and clarified.

To obtain a simplified picture of the burning process, the following assumptions will be made:

1. Terminal conditions.
 - a. The charge enters the kiln at 100°C and leaves at 1400°C .
 - b. The combustion gases are obtained from burning carbon and contain 21% CO_2 and 79% N_2 .
 - c. On the basis of the data of Illustration 5 the amount of stack gas leaving the kiln of Illustration 6 is estimated to be 11 mols per 100 lb of clinker and its temperature 1100°C .*
2. Heating of the solid stream.
 - a. At any given cross section of the kiln the charge is uniform in temperature.
 - b. All decomposition of MgCO_3 occurs at 540°C and all decomposition of CaCO_3 at 900°C . The third stage of reaction begins at 1000°C and the final stage at 1300°C .
 - c. The exothermic reactions are completed almost instantaneously and in each case the heat of reaction is immediately absorbed by the charge to increase its sensible-heat content.
 - d. The specific heat of the charge is 0.25 from 100 to 540°C and 0.29 from 540 to 1300°C .
 - e. Loss of water, dust, and alkali to the gas stream is ignored.
 - f. The effect of temperature on heat of reaction is neglected.
3. Cooling of the gas stream.
 - a. At any given cross section of the kiln the gas is uniform in temperature.
 - b. The gas passes through the kiln unchanged in amount. In other words, the effect of evolution of CO_2 , etc., from the charge on the amount and heat capacity of the gas stream is neglected.

* The reported temperature of the stack gas in Illustration 5 is abnormally low because of excessive heat losses from the kiln and the effect of radiation on the reading of the thermocouple. Hence, a somewhat higher value has been chosen in this case.

- c. The heat content of the gases entering the product-discharge end is equal to the heat in the fuel and air supplied to the kiln plus heat recovered from the hot clinker less the heat losses from the kiln to the surroundings. This is equivalent to saying that all the heat lost from the kiln to the surroundings is lost from the pre-heater or the hot *end* of the kiln and no heat is lost through the cylindrical walls.
- d. Radiation from the hot end of the kiln to any intermediate section is equal to the radiation from this section to the cold end of the kiln.
- e. The effect of water, dust, and alkali is neglected.

With the aid of these assumptions one can easily determine the relationship between the temperatures of the solid and gas streams at any point in the kiln and the amount of heat transferred from gas to solid between the feed end and the point in question. For example, the heat required to raise the charge from the inlet temperature to 540°C equals $[100 + (1.051)(44)](0.25)(540 - 100) = 16,100$ Chu. Since the specific heat is assumed to be constant, the relation between heat and temperature over the interval from 100 to 540°C is linear. At 540°C , decomposition of MgCO_3 proceeds with the absorption of 1650 Chu at constant temperature. Hence, the total amount of heat transferred to the solid stream between the feed end of the kiln and the point at which decomposition of MgCO_3 is completed is $16,100 + 1650 = 17,750$ Chu. The results of similar calculations for the entire process of heating the solid and cooling the gas are shown in Fig. 8-5.

Note that Fig. 8-5 is exactly the same in principle as Fig. 3-8 (page 73). In the latter case the discontinuity in one of the curves is caused by a simple change in phase from the gaseous to the liquid state. In Fig. 8-5 the discontinuities indicate phase changes resulting from chemical action.

How closely do the idealized curves in Fig. 8-5 agree with the actual situation in the kiln? First, consider the terminal conditions. The actual conditions will of course vary somewhat with the fuel, the nature of the raw materials, etc. However, the assumed conditions are reasonably representative for a coal-fired cement kiln with a length of 100 ft, equipped with good insulation. The heating of the solid requires closer study. Basically, the construction of the lower line in Fig. 8-5 involves the assumption that the reaction zones within the kiln are sharply distinct and no overlapping occurs. In actual fact, Figs. 8-3 and 8-4 reveal that there is a considerable amount of overlapping. One can say, therefore, that the lower line of Fig. 8-5 is correct in its delineation of major trends but in error in that it fails to indicate the existence of transition regions between the major zones. The actual heating curve

must be characterized by transitions from one straight-line region to another, instead of by the sharp breaks of Fig. 8-5. The principal uncertainty in the upper curve of Fig. 8-5 is at the product-discharge end of the kiln (the right-hand end of the curve), where the greatest amount of heat is being lost from the kiln and radiation effects are large. About all that can be said is that if heat is in fact being lost through the cylindrical walls of the kiln the actual temperature of the gas stream must lie above the upper curve of Fig. 8-5 and below the theoretical flame temperature. As the gas is cooled and radiation effects and the rate of heat loss through the cylindrical walls drop off, the actual curve for the gas approaches the idealized curve of the figure. Figure 8-5, then, is not a

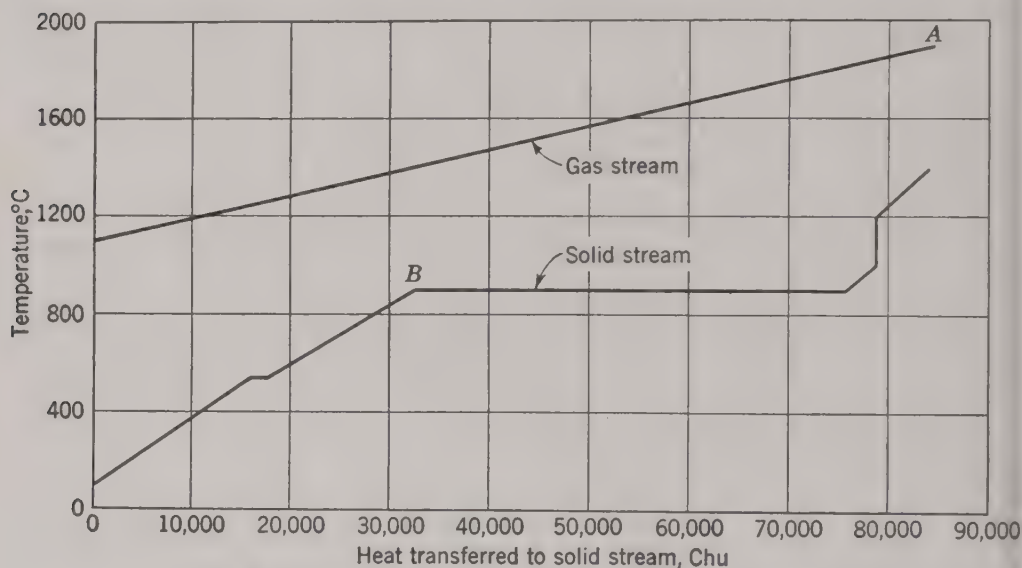


FIG. 8-5. Idealized cement kiln. Basis: 100 lb of clinker.

detailed drawing; it is a sketch, revealing major traits of character. A brief study of the figure from this point of view proves highly informative.

Doubtless the most striking aspect is what it shows about the temperature difference between the gas and solid streams. At no point is this difference less than several hundred centigrade degrees. Obviously, heat transfer from the gas to the solid is not being blocked by temperature-equilibrium limitations of the type described in Chap. 3. The blame for the high temperature of the stack gas and the correspondingly poor economy of fuel must lie elsewhere.

While the temperature difference between the main stream of gas and the main stream of solid is appreciable at all points along the length of the kiln, it is smallest at the point at which decomposition of CaCO_3 begins. Thus, at the start of decomposition, Fig. 8-5 shows a temperature difference of $1400 - 900 = 500$ degrees. At the end, the difference is

$1800 - 900 = 900$ degrees, or almost double. The corresponding percentage increase in the rate of heat transfer from gas to solid is greater than this, since much of the heat transfer in the kiln, especially at the hot end, is by radiation, in which the rate is proportional not to temperature difference but to the difference of the fourth powers of the absolute temperatures. Obviously, the situation is too complicated to permit the development, without further information, of any quantitative relation of temperature differences derived from Fig. 8-5 with heat transfer and the rate of decomposition of CaCO_3 , plotted in Fig. 8-3. However, the trend of the temperature differences in Fig. 8-5 must account, at least in part, for the increasing rate of decomposition of CaCO_3 as decomposition proceeds.

A third point to notice about Fig. 8-5 is that the lower curve, the heating curve for the solid, will remain in essentially the same position on the diagram for all normal conditions of operation. No matter what the operating conditions are otherwise, the solid stream must be heated to a temperature in the neighborhood of 1400°C if the formation of tricalcium silicate is to be carried to completion, and if this is done, the same amount of heat must be supplied per 100 lb of clinker and at the same temperature levels as indicated in the figure.

Note also that the location of the right-hand end of the upper curve (point A on Fig. 8-5) is quite insensitive to changes in operation of the kiln. This is true because the temperature of the combustion gases entering the kiln is determined primarily by the heat of combustion of the fuel and the specific heat of the combustion products, *i.e.*, by factors that are related to the theoretical flame temperature and are not affected by changes in throughput or the ratio of fuel to product. The other energy effects that influence the temperature of the gases entering the kiln are normally secondary. Thus, the data of Illustration 5 show that the heat supplied to the incoming air by the clinker is of the order of 10% of the heat of combustion. With well-insulated kilns the heat losses to the surroundings are somewhat larger than this but still fairly small compared to the total heat input as chemical energy in the fuel. The heat recovered by preheating the air and the heat losses almost cancel each other, with the result that the temperature at point A is usually fairly constant within the normal range of operating conditions.

In Fig. 8-5 the variable most responsive to a change in conditions is the slope of the upper curve. The slope of this curve, which represents the cooling of the gas stream as it flows through the kiln, is directly affected by the relation between the heat capacities of the gas and solid streams, and this in turn depends on the ratio of fuel to product, *i.e.*, the fuel consumption. If the fuel consumption is high, the heat capacity of the gas stream is correspondingly high and the slope of the upper curve

is low. If the fuel consumption is low, the reverse is true. Therefore, in terms of Fig. 8-5, the net result of a decrease in the fuel consumption is to shift the upper curve in such a way that the right-hand end is in nearly the same position as before, while the rest of the curve drops off more steeply from right to left. As may be seen by a study of the figure, a shift of the upper curve in the manner described has the effect of decreasing the temperature difference between the gas and solid streams at all points in the kiln.

To the engineer the importance of the above conclusion is great. He is compelled to realize that, whatever steps he may take in an effort to reduce fuel consumption, he will have to reckon with the existence of lower temperature differences within the kiln and therefore with a lower driving force for the transfer of heat. Practically, there are a number of ways in which an adjustment can be made for this reduction in driving force. One possibility is a reduction in the amount of raw mix handled by the kiln per unit time, a step which has the effect of reducing the amount of heat that must be transferred per unit time. Improvement in fuel consumption is thus gained at the expense of capacity. If, on the other hand, one wishes to have a low fuel consumption and a high kiln capacity at the same time, one can either install devices to mix the gas and solid streams more vigorously or increase the area available for heat transfer by building a longer kiln.

If one continues to reduce the ratio of fuel to product, a condition is eventually reached in which the gas curve approaches the solid curve at some point, resulting in a temperature-equilibrium limitation or "bottle-neck" of the sort discussed in Chap. 3. In the present case, if one uses the lowest possible ratio, the location of the gas curve is roughly approximated by a straight line through points *A* and *B* on Fig. 8-5.

To summarize, the data of Lacey and Shirley make it plain that the high temperature of the stack gas in Illustration 5 is not the result of temperature-equilibrium limitations within the kiln. The kiln is short and is being operated with a high stack-gas temperature in order to maintain a high rate of production of cement. If greater economy of heat is desired, it can be achieved by (1) reducing the heat losses from the kiln to the surroundings, (2) adding a waste-heat boiler, (3) reducing capacity, (4) installing devices to increase the intimacy of contact of the gas and solid streams, or (5) building a longer kiln. Whether some such change is justified will depend on the cost of the change and the value of the fuel saved.

As to reaction mechanism, the data show that decomposition of CaCO_3 is a comparatively slow reaction. While the fractional rate of decomposition increases as reaction proceeds, until the CaCO_3 is entirely consumed, the increase is not large as chemical reactions go, and the process

appears to be limited by the rate at which the large endothermic heat of reaction can be supplied to the surface of the CaCO_3 . So long as CaCO_3 is present in significant amount, the fractional rate of reaction of free lime with the rest of the charge is low and remarkably constant. However, in the same zone of the kiln in which CaCO_3 finally disappears, reaction of free lime with the rest of the charge becomes very rapid. The conclusion is obvious that the increase in the rate of reaction of free lime is due to a pickup in temperature, which occurs as soon as CaCO_3 has largely disappeared. The figures indicate that two stages are involved in the clinker-forming reactions.

Limited though the data of Lacey and Shirley are, they yield a wealth of information that is of value in securing not only better operation of old equipment but also better design of new.

PROBLEMS

1. Limestone is being calcined in a rotary kiln fired with coke breeze. The flue gas contains 31.3% CO_2 , 1.8% O_2 , and no CO or H_2 . The analysis of the stone is 51.0% CaO , 2.0% MgO , 42.2% CO_2 , 1.5% Al_2O_3 , 1.2% SiO_2 , and 2.1% H_2O . The coke is hydrogen-free and dry and contains 8% ash. The gases leave the kiln at 860°F and the lime at 950°F. Calculate the following:

(a) The pounds of lime produced and the cubic feet of air fed at 70°F and 760 mm Hg per pound of coke.

(b) The percentage of the heating value of the coke accounted for as chemical heat of decomposition, sensible heat in the stack gas, sensible heat in the lime, and losses to the surroundings through the walls of the kiln.

2. A vertical shaft kiln, 80 ft high and with a maximum outside diameter of 24 ft, is charged with 380 to 400 tons/day of dolomite (predominantly $\text{CaCO}_3\cdot\text{MgCO}_3$) and 145 lb coke per ton of stone.¹ The stone contains 52.8% CaCO_3 , 46.0% MgCO_3 , 0.33% SiO_2 , and 0.10% R_2O_3 ; and the coke analysis averages 12% moisture and 12% ash. The heating value of the coke is 11,100 Btu/lb. The lime product leaves the bottom of the kiln at 160°F and contains 2.0% CO_2 . The lime also contains an amount of unburnt carbon equal to 3.7% of the carbon in the coke charged. The average temperature of the air entering the bottom of the kiln is 70°F. The top gas leaves at 120°F and contains 43% CO_2 (dry basis) and negligible CO and H_2 .

(a) Calculate from the above data the complete Orsat analysis of the top gas and the cubic feet per minute of air supplied to the kiln, measured at 60°F and 1 atm.

(b) Compute the Btu evolved by combustion of the coke actually burnt, the Btu consumed in decomposition, the Btu lost as sensible heat in the dry top gas, the Btu lost as sensible and latent heat in the water vapor in the top gas, the Btu lost as sensible heat in the lime, and by difference the Btu lost to the surroundings through the walls of the kiln, expressing all results on a basis of 1 ton of stone charged.

Assume that the dolomite charged to the kiln is a mixture of $\text{CaCO}_3\cdot\text{MgCO}_3$ and MgCO_3 and that decomposition proceeds in three stages: first, decomposition of $\text{CaCO}_3\cdot\text{MgCO}_3$ to form CaCO_3 and MgCO_3 (heat of decomposition = 7600 cal per g mol of $\text{CaCO}_3\cdot\text{MgCO}_3$ decomposed); second, decomposition of MgCO_3 (heat of decomposition = 23,800 cal/g mol); and finally, decomposition of CaCO_3 (heat of

¹ C. C. Brumbaugh, *Chem. Eng. Progr.*, 44, 881 (1948).

decomposition = 43,700 cal/g mol). Residual CO_2 in the lime may be ascribed to the presence of undecomposed CaCO_3 . The average specific heats of CaO and MgO between 70° and 160°F are 0.19 and 0.23, respectively.

(c) By measurements and calculations entirely different from those involved in the calculations of parts (a) and (b) (except for measurement of the per cent CO_2 in the gas), the analysis of the top gas has been found to be 43% CO_2 , 1.3% O_2 , and 55.7% N_2 , the air-flow rate has been determined to be between 5000 and 6000 cu ft/min, and the loss of heat to the surroundings is estimated at 90,000 Btu per ton of stone. In the light of these facts, what is your opinion of the reliability of the data available on the performance of this kiln?

3. A plant is burning a limestone analysis of which indicates 51.5% CaO , 2.6% MgO , 43.4% CO_2 , and 1.1% moisture. The kiln is fired with a natural gas the combustion analysis of which shows 94% CH_4 and 6% C_2H_6 . The operation of the kiln is such that the lime is incompletely burnt, but this is not a serious matter for the purpose for which the product is to be used. This lime contains 6.4% CO_2 . The top gas is sampled half-hourly for a 12-hr period, and the average analysis is found to be 18.57% CO_2 , 1.93% O_2 , and 79.5% N_2 .

(a) Calculate the pounds of burnt lime produced by this kiln per 1000 cu ft of fuel gas consumed, d.s.c.

(b) The plant operating the kiln uses the same natural gas as fuel in another kiln, burning the same stone. The gas from the second kiln analyzes 17.0% CO_2 , 9.76% O_2 , and 73.24% N_2 . The burnt lime from this kiln carries a negligible amount of residual CO_2 . The plant is well managed and well operated, and there is every reason to believe that both kilns are being operated intelligently and effectively. Granting these premises, what conclusions do you draw as to the two kilns in the light of the facts given?

4. A calcination pilot plant manufacturing 11 tons/day of lime consists of three compartments, one above another, in a vertical shaft 5 ft in diameter.¹ Each compartment contains a fluidized bed. The middle bed, which is maintained at a temperature of 1700 to 1750°F , is the calcination zone, while the top bed serves to exchange heat between the hot gases leaving the calcination zone and the cold limestone feed, and the bottom bed to exchange heat between the hot lime leaving the calcination zone and the cold air entering the bottom of the kiln. The average temperature of the top bed is 1100°F and that of the bottom bed 500 to 550°F . The bottom bed is fluidized by the air supplied to the kiln, the middle bed by the preheated air from the bottom bed, and the top bed by the hot gases from the middle bed. The charge (a crystalline limestone) is fed continuously to the top bed, preheated stone overflows continuously from the top bed to the middle one, hot lime overflows from the middle bed to the bottom one, and the lime product is withdrawn continuously as overflow from the bottom bed. The fuel is Bunker C fuel oil, which is injected continuously into the middle bed at the rate of 43 gal per ton of lime. The product is a high-quality lime and contains less than 1% CO_2 .

As an aid to study of this operation, the following simplifying assumptions are recommended: (1) The stone is pure CaCO_3 and the lime pure CaO . According to Kelley,² the heat capacity of pure CaCO_3 in cal/(g mol)(deg K) is $19.68 + 0.01189T - (307,600/T^2)$ and that of pure CaO is $10.00 + 0.00484T - (108,000/T^2)$, where T is in degrees Kelvin. (2) The analysis of the oil is 88% C and 12% H, its heating value 19,000 Btu/lb, and its density 7.9 lb/gal. (3) Mixing in the fluidized beds is sufficiently perfect so that the gas and solid streams leaving the top bed are at 1100°F ,

¹ R. P. Kite and E. J. Roberts, *Chem. Eng.*, **54**, 112 (1947).

² K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934).

those leaving the calcination zone at 1725°F, and those leaving the bottom bed at 525°F. (4) The bottom bed is sufficiently well insulated and at a low enough temperature so that heat losses from it to the surroundings can be neglected. (5) The stone, oil, and air enter at 60°F. (6) The gases leaving the middle bed contain negligible CO and H₂.

(a) Calculate the per cent CO₂ in the top gas and the per cent excess air employed in burning the oil.

(b) A sketch in the reference cited indicates that the calcination compartment is approximately 7 ft high. Estimate the heat losses through the walls of this compartment in Btu/(hr)(sq ft).

5. A plant consisting of five identical vertical lime kilns was tested over a 12-hr period under normal operating conditions to determine its performance. Each kiln was 63 ft high and had an outside diameter of 10 ft. The kilns were housed in a building 40 ft high. Below the roof, the average temperature of the outside shells of the kilns was 296°F; above the roof, the average temperature was 120°F. The average analysis of the charge was 97.5% CaCO₃. The total production of lime from all five kilns during the 12-hr period was 139,500 lb, and the average analysis 93% CaO, 3.8% core, and 3.2% inerts. The average temperature of the lime at the fire boxes was 1920°F and at the discharge table 569°F. The fuel was producer gas, which entered the kilns at an average temperature of 787°F. The producer gas contained 7.9% CO₂, 1.0% O₂, 18.4% CO, 3.7% CH₄, 12.1% H₂, and 56.9% N₂; and its dew point was 112°F. The average composition of the top gas was 22.4% CO₂, 5.6% O₂, 0.3% CO, and 71.7% N₂; and its temperature averaged 626°F. The air entered the bottom of the kiln at an average temperature of 60°F, carrying 0.0046 lb H₂O per pound dry air. Calculate the following quantities:

(a) Mols of dry producer gas per ton lime.

(b) Mols of dry air per ton lime.

(c) Mols of dry top gas per ton lime.

(d) Mols of H₂O in the top gas per 100 mols dry gas.

(e) Per cent excess air.

(f) Btu lost to the surroundings through the walls of the kilns per ton of stone.

To what factor or factors do you attribute the difference between the heat loss from these kilns and the estimated loss of 90,000 Btu per ton of stone from the kiln of Prob. 2?

(g) What suggestions, if any, can you make for improving the operation of the plant?

6. Plaster of paris (calcium sulfate hemihydrate, CaSO₄·½H₂O) is being manufactured by the low-temperature calcination of gypsum (calcium sulfate dihydrate, CaSO₄·2H₂O) in a well-lagged rotary kiln. The source of heat for calcination is a stream of hot air passing through the kiln. The department superintendent gives the following data as representative of operation: Gypsum enters the kiln at 25°C. Air enters the opposite end at about 300°C and leaves at 100°C. The calcined product, averaging 1000 lb of plaster per hour, leaves at around 210°C.

The heat of conversion of the dihydrate to the hemihydrate and water vapor at 25°C is 23,500 cal/g mol. The equilibrium pressure of the reaction is 1 atm at 101.5°C, but the rate of decomposition of gypsum at atmospheric pressure becomes appreciable only at temperatures above about 130°C. The decomposition pressure of the hemihydrate is 1 atm at about 200°C, but the rate of decomposition is very low below 300°C. The specific heat of the dihydrate is approximately 0.27 and of the hemihydrate 0.24.

(a) Estimate the hot-air requirement of the kiln, expressed as pound mols per hour.

(b) Plot the temperature in degrees centigrade of the solid stream flowing through

the kiln vs. the amount of heat transferred to the solid stream in Btu per pound mol of dihydrate charged. Assume that all decomposition takes place at 130°C .

(c) To the plot of part (b), add a curve showing the temperature of the air stream in degrees centigrade vs. the amount of heat transferred to the solid stream in Btu per pound mol of dihydrate charged. Assume that the water vapor driven from the solid does not mix or exchange heat with the air in the region of the kiln in which decomposition is occurring but mixes completely with the air as soon as it leaves this region.

7. A large vertical shaft kiln is to be designed to burn a high-grade limestone with producer gas. The composition of the gas is expected to be approximately 5% CO_2 , 25% CO , 30% H_2 , and 40% N_2 , with a partial pressure of water vapor of 30 mm Hg; and 5% excess air will be employed. The gas will be delivered to the eyes of the kiln at about 800°F .

The following simplifying assumptions have been agreed upon as a basis for studying the characteristics of the proposed operation: (1) The charge will be considered to be pure CaCO_3 and the lime pure CaO . (2) Both stone and air will be assumed to enter the kiln at 60°F . (3) Heat losses to the surroundings will be neglected. (4) The specific heats of CaCO_3 and CaO will be considered to be 0.28 and 0.24, respectively, independent of temperature, and the molal heat capacities of CO_2 , H_2O , O_2 , and N_2 will be considered constant and equal to 14, 11, 9, and 8, respectively. (5) Dissociation of CO_2 and H_2O and formation of NO in the combustion products will be neglected. (6) In line with the solution to Illustration 6, the proposed kiln will be considered to have four distinct zones. These will be, first, a charge-preheat zone in which the descending charge is preheated without significant decomposition to 950°C by heat exchange with the hot gases from the combustion zone; second, a decomposition zone in which the stone is completely decomposed at a constant temperature of 950°C by means of heat obtained from the gases flowing up the shaft; third, a combustion zone in the neighborhood of the eyes of the kiln, in which combustion is complete and which is so narrow (in the vertical direction) that no appreciable transfer of heat from the gases to the solid stream occurs within it; and finally, an air-preheat zone in which the lime descending from the combustion zone at 950°C gives up heat to the ascending air. The CO_2 evolved by the stone will be assumed to flow upward through the decomposition zone without mixing or heat exchange with the combustion products until it reaches the upper boundary of the decomposition zone, at which point it will be completely mixed with the combustion products.

(a) Make a plot of the stone temperature in degrees Fahrenheit in the stone preheat and decomposition zones vs. the quantity of heat transferred to the stone in Btu per pound of CaCO_3 .

(b) Make a plot of the lime temperature in degrees Fahrenheit in the air preheat zone vs. the quantity of heat transferred from the lime to the air in Btu per pound of CaO .

(c) What is the minimum possible ratio of fuel to product in this kiln, expressed as mols of dry producer gas per ton of CaO ?

(d) Using the minimum ratio of gas to product, show on the plot of part (a) a curve representing the temperature of the gas vs. the quantity of heat transferred to the stone and on the plot of part (b) a curve representing the temperature of the air vs. the heat lost by the lime.

8. During a representative 7-hr period of steady operation an oil-fired rotary cement kiln in California consumed 124,300 lb of feed and produced 79,670 lb of clinker, together with 4830 lb of dust deposited in the stack chamber and 820 lb of dust recovered by electrical precipitators.¹ The analyses of the various streams are given below in weight per cent.

¹ W. N. Lacey and H. Woods, *Ind. Eng. Chem.* **27**, 379 (1935).

Constituent	Kiln feed	Clinker	Stack dust	Treater dust
SiO ₂	14.7	22.3	12.0	11.8
Al ₂ O ₃	3.7	6.0	3.4	2.7
Fe ₂ O ₃	1.4	2.2	1.2	1.3
CaO.....	43.6	63.8	55.7	56.3
MgO.....	3.6	5.2	4.5	4.1
SO ₃	5.0	6.8
Loss.....	32.3	0.2	14.2	12.4
Total.....	99.3	99.7	96.0	95.4

The kiln feed was a mixture of limestone and clay. Special analysis of the feed showed that the 32.3% loss on ignition was 29.1% CO₂ and 3.2% H₂O. However, the moisture removable by drying at 105°C was only 0.2%, indicating that most of the water in the feed was combined with the clay. The low totals of the last two analyses are undoubtedly due to the presence of alkalies, which were not determined. Estimate the following quantities:

(a) The composition of the total solid product (*i.e.*, the clinker plus dust) in terms of the chemical compounds actually present. Express the amount of each compound as mols per 100 lb of clinker plus dust.

(b) The Btu evolved per pound of total solid product formed, if the total solid product is considered to be formed at 25°C from the constituent oxides, present originally solely as oxides.

(c) The composition of the kiln feed in terms of the chemical compounds actually present. Express the amount of each compound as mols per 100 lb of clinker plus dust.

(d) The over-all heat of reaction in the kiln in Btu per 100 lb of clinker plus dust. The heat required for dehydration of the clay was estimated to be 4000 Btu per lb of water removed.

Chapter 9

FIXED ALKALIES

In the fixed-alkali industry there are a number of operations in which success depends upon understanding the chemistry of solutions. The chemical systems involved are sometimes quite complex, and the principles of stoichiometry can be of invaluable assistance in determining the nature of the reactions and aiding in their control. A relatively simple example is the causticization of soda ash.

Illustration 1. A small manufacturer undertakes a new commitment, which involves the preparation of a caustic-soda solution by causticizing a solution of soda ash (practically pure Na_2CO_3) with lime. As he is unfamiliar with the operation, he employs a locally available dolomitic lime, analyzing 66.5% CaO and 21.6% MgO . The soda-ash solution is 2.69 N and has a specific gravity of 1.126. It is imperative that the conversion of carbonate to caustic be not less than 98% in order for the product to be satisfactory for the use intended.

In his first trial run the manufacturer uses 225 lb of lime and 240 U.S. gallons of soda-ash solution. The mixture is boiled for 1 hr and then allowed to settle. Analysis of the clear, supernatant solution for Na_2CO_3 and NaOH discloses that it is now 3.01 N and only 89.0% of the alkali in the solution is in the form of NaOH . On the theory that he may not have been using enough lime, the manufacturer makes a second run, using 600 lb of lime instead of 225. The composition of the clear liquor is found to be substantially the same as before.

At this point you are called in to assist. What do you think is the trouble, and what do you recommend be done about it?

Discussion. The quantities of materials, expressed as volumes of solution and weights of solid, do not reveal what is happening chemically. A better orientation is obtained if one converts the input of the reactants to mols and compares them with the stoichiometrical proportions of the reaction $\text{Na}_2\text{CO}_3 + \text{R}(\text{OH})_2 = 2\text{NaOH} + \text{RCO}_3$. On a basis of 240 gal of initial solution, the input of Na_2CO_3 is

Gal	Cu ft	Liters	G eq	Lb eq	
240	1	28.3	2.69	1	$\frac{1}{2} = 2.69 \text{ lb mols}$
	7.48			454	

The supply of CaO and MgO in the first run is

$$225[(0.665/56) + (0.216/40)] = 3.89 \text{ mols}$$

These figures make clear that even in the first run an appreciable excess of hydroxide was used. Since $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are only sparingly soluble, the excess ensured that solid $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were in contact with the final solution. This explains why larger quantities of lime in the second run had no noticeable effect on the concentrations in the liquid phase. The concentration of hydroxyl ion in the solution could not be increased by adding solid lime, because the concentration had already reached the upper limit imposed by equilibrium.

It is instructive to consider the equilibrium situation first from the point of view of the phase rule.¹ Neglecting for the moment the complications due to presence of MgO in the lime, one can visualize a system containing solid $\text{Ca}(\text{OH})_2$ and solid CaCO_3 in equilibrium with an aqueous alkali solution and gaseous CO_2 as being made up of four components, Na_2CO_3 , $\text{Ca}(\text{OH})_2$, H_2O , and CO_2 , the latter being gained from or lost to the vapor phase. There are four phases: two solid, one liquid, and one vapor. If one fixes the temperature and the concentration of sodium ion in the solution, the system is, according to the phase rule, nonvariant. That is, so long as all the above conditions apply, the concentrations of all constituents in the liquid phase must remain the same even though the relative amounts of the four phases may be changed. Since the temperature cannot be raised above the atmospheric boiling point without the installation of expensive equipment constructed to withstand pressure, the only practicable method of removing one of the above restrictions is to change the concentration of sodium ion in the solution. This can be done by varying the strength of the initial solution of Na_2CO_3 .

¹ The principle known as the phase rule states that in any system the sum of the number of phases P and of the variance V is greater by two than the number of components C ; that is,

$$P + V = C + 2$$

The "variance" of a system, which is also called the "degrees of freedom," is defined as the number of independently variable quantities, such as pressure, temperature, and composition, that must be specified in order to define the system completely, *i.e.*, to determine or fix the intensive properties of each phase of the system, such as density, index of refraction, and specific conductance. The number of components C is the least number of independently variable chemical substances that must be specified so that the composition of each phase of the system will be fully determined. In phase-rule considerations the term "system" never means a selected or particular system but the full series of "systems" of the same qualitative but varying quantitative composition that can be made from the components. For further discussion, including definitions of terms used in describing phase problems, see any standard text on physical chemistry.

The direction in which to move in the attempt to increase conversion is made plain by a consideration of solubility products. Let (Na^+) , (Ca^{++}) , $(\text{CO}_3^{=})$, and (OH^-) represent the concentrations of sodium, calcium, carbonate, and hydroxyl ions, respectively, in gram ions per liter. In a solution in equilibrium with solid $\text{Ca}(\text{OH})_2$ at a given temperature, the law of mass action requires that the product $(\text{Ca}^{++})(\text{OH}^-)^2$ be constant. Let this constant be K_1 . Similarly, in a solution in equilibrium with solid CaCO_3 , the product $(\text{Ca}^{++})(\text{CO}_3^{=}) = K_2$. In the case under discussion, the solution is in equilibrium with both solids, and therefore both equations apply simultaneously. Division of the first by the second gives the result $(\text{OH}^-)^2/(\text{CO}_3^{=}) = K_1/K_2$. The ratio of K_1 to K_2 is a third constant, which may be denoted by K . It will be noted that the equilibrium constant K equals the product of (OH^-) and $(\text{OH}^-)/(\text{CO}_3^{=})$. If this product is to remain constant, then as (OH^-) approaches zero the ratio $(\text{OH}^-)/(\text{CO}_3^{=})$ must approach infinity. In other words, the conversion of carbonate to caustic, which can be measured by the ratio $(\text{OH}^-)/(\text{CO}_3^{=})$, is favored by low concentrations. It follows that the way to improve conversion in this instance is to use a more dilute soda-ash solution.

A quantitative relation between concentration and conversion can be derived algebraically. Since all sodium ions in the final solution come from Na_2CO_3 feed, the per cent conversion of Na_2CO_3 to NaOH is equal to $100(\text{OH}^-)/(\text{Na}^+)$. Let the per cent conversion equal C . Remembering that the negative and positive ions in the solution must be equivalent, one can set up three simultaneous equations, as follows:

$$\begin{aligned}(\text{OH}^-)^2/(\text{CO}_3^{=}) &= K \\ 100(\text{OH}^-)/(\text{Na}^+) &= C \\ (\text{Na}^+) &= (\text{OH}^-) + 2(\text{CO}_3^{=})\end{aligned}$$

Solving for C in terms of K and (Na^+) , the result is that

$$C = \frac{100 \sqrt{K^2 + 8K(\text{Na}^+)} - 100K}{4(\text{Na}^+)}$$

The characteristics of this relation may be explored by considering what happens when the solution is infinitely dilute, *i.e.*, when $(\text{Na}^+) = 0$. In this case, the fraction on the right-hand side of the equation is found to be indeterminate. However, application of standard mathematical methods shows that the limiting value of the fraction as (Na^+) approaches zero is equal to 100.

The value of K is obtained by utilizing data on the solubility products of CaCO_3 and $\text{Ca}(\text{OH})_2$. According to Seidell,¹ the concentration of

¹ A. Seidell, "Solubilities of Inorganic and Organic Compounds," 2d ed., Vol. I, p. 191, D. Van Nostrand Company, Inc., New York, 1919. See also *ibid.*, 3d ed., Vol. I, p. 264, 1940.

Ca^{++} in aqueous solution saturated with CaCO_3 at 16°C and under a partial pressure of CO_2 of 0.0003 atm is 5.79×10^{-4} ions per liter, while the concentration of CO_3^{--} in the same solution is 0.17×10^{-4} ions per liter. From these figures,

$$K_1 = (5.79 \times 10^{-4})(0.17 \times 10^{-4}) = 9.85 \times 10^{-9}$$

The same reference gives the solubility of Ca(OH)_2 in water at 25°C as 0.159 g per 100 g of water; $0.159(10)/74 = 2.15 \times 10^{-2}$ ions of Ca^{++} per liter; the OH^- ions are double in number, and

$$(2.15 \times 10^{-2})(4.30 \times 10^{-2})^2 = 3.98 \times 10^{-5} = K_2$$

It follows that $K = 3.98 \times 10^{-5}/9.85 \times 10^{-9} = 4000$. Substitution of this value for K in the equation for C gives the relation between C and (Na^+) . For example, in a solution having a normality of 3.01, which was the concentration used in the trial runs,

$$C = \frac{100 \sqrt{(4000)^2 + 8(4000)(3.01)} - 100(4000)}{4(3.01)}$$

which turns out to be greater than 99%.

In actual fact, the conversion which the manufacturer secured was only 89.0%, even though the negligible effect of additional lime indicates that an approach to equilibrium prevented further reaction. This discrepancy may conceivably have been due to any one of several factors or a combination of them. For example, attainment of equilibrium may have been apparent rather than real, because of extremely low reaction rate near the end of the operation. Equilibrium may have been reached in the boiling, agitated solution, but equilibrium with the solid phase may not have been reached in the settled, cooler solution. Again, the conversion may have been lower than otherwise because of imperfect protection of the solution from contact with the atmosphere and consequent absorption of CO_2 . The presence of MgO in the lime undoubtedly affects the equilibrium to some extent. Finally, the activity of Ca^{++} , CO_3^{--} , and OH^- in a caustic solution may be significantly different from the activities in dilute aqueous solutions, such as those of the experiments in which the solubility products were determined.

If the manufacturer is to be given sound advice, it is desirable to ascertain, if possible, the relative importance of the various factors listed above. The effect of change in temperature on equilibrium may be discarded as a major factor because to explain a conversion as low as 89% a change of more than 100-fold in the equilibrium constant K is necessary, and this is deemed to be unlikely. Some clues to the situation may be found by reference to the scientific literature. For example, laboratory experiments on causticization of soda-ash solutions have been

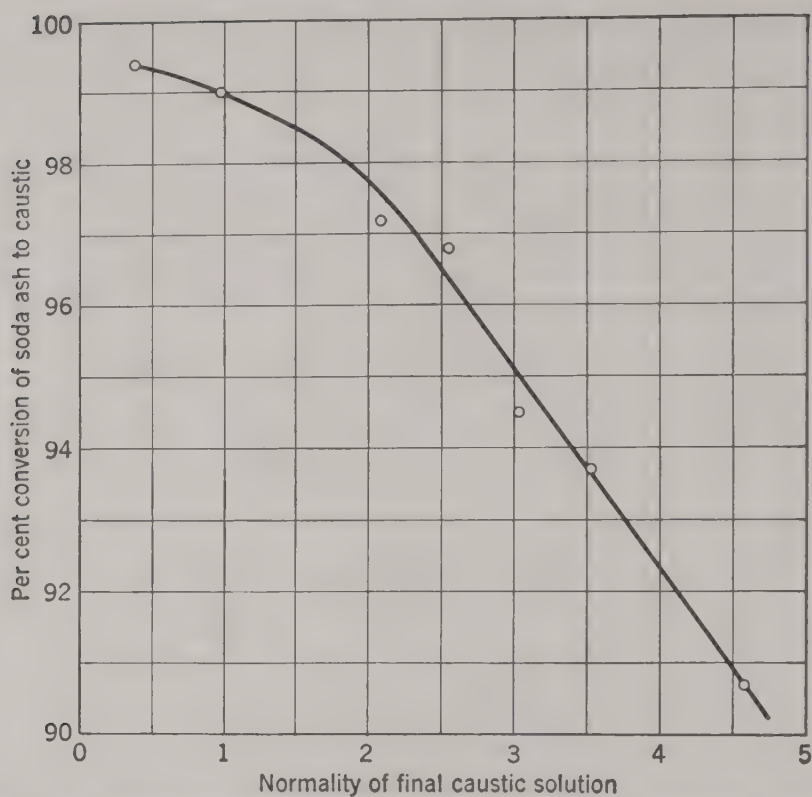


FIG. 9-1. Data of Lunge on causticization of soda-ash solutions. Normality is expressed with respect to $\text{NaOH} + \text{Na}_2\text{CO}_3$.

reported by Lunge,¹ whose results are tabulated below and shown graphically in Fig. 9-1.

Normality of final caustic solution	Per cent conversion of soda ash to caustic	$\frac{(\text{OH}^-)^2}{(\text{CO}_3^{--})}$
0.39	99.4	127
0.97	99.0	191
2.08	97.2	141
2.55	96.8	149
3.04	94.5	99
3.52	93.7	98
4.58	90.7	81

At a normality of 3.01, Fig. 9-1 shows a conversion of 95%, somewhat higher than the 89% conversion obtained by the manufacturer. Inasmuch as the experiments of Lunge were performed with $\text{Ca}(\text{OH})_2$ instead

¹ G. Lunge, "Sulfuric Acid and Alkali," 3d ed., Vol. II, part 2, p. 807, Table A, Exp. I, Gurney and Jackson, London, 1909.

of a dolomitic lime and under laboratory conditions facilitating adequate provision against absorption of CO_2 from the air during handling, the difference between the two figures is a good index of the combined effect of MgO in the lime and absorption of CO_2 . It should be possible for the manufacturer to improve his conversion materially by purchasing a non-dolomitic lime and taking steps to prevent contact of the caustic solution with air. However, in addition to these steps, it will be necessary according to Fig. 9-1 to dilute the soda-ash solution to somewhat less than 2 N , if a conversion as high as 98% is to be secured. The exact degree of dilution required for the particular lime employed will have to be determined by trial runs in the plant.

If the difference between Lunge's data and the conversion predicted from solubility products were due primarily to a difference between the activities of the various ions in dilute aqueous solutions and relatively concentrated caustic solutions, the calculated and observed conversions ought to approach each other as the normality of the final caustic solution decreases. In the limiting case of zero normality, the two conversions should be identical and equal to 100%. However, the data of Fig. 9-1 show a trend toward intersection with the y axis at a conversion less than 100%. This trend is admittedly slight, but the point is confirmed and emphasized by the values of the apparent equilibrium constant $(\text{OH}^-)^2/(\text{CO}_3^{=})$, which is a far more sensitive index of the behavior of the solutions than is conversion. The calculated value of K , it will be recalled, is 4000. By contrast, all the values observed by Lunge fall below 200, and far from tending toward a value of 4000 at zero concentration, these data indicate that K in the most dilute solution tested was lower than K in more concentrated solutions. The conclusion is plain that effect of concentration on ionic activity does not account for the low conversions observed in Lunge's experiments. The explanation must be in extremely low reaction rates at high conversions or an equilibrium of an unknown character.

Illustration 2. In a test performed by students at the Bangor station of the M.I.T. School of Chemical Engineering Practice, information was secured on the operation of an Allen-Moore cell. The effluent liquor was found to contain 110 g of NaOH , 170 g of NaCl , 1.1 g of NaClO_3 , and negligible NaClO per liter. The voltage on the cell was 3.8, and the current consumption was 88,000 amp-hr per cubic meter of effluent liquor. The gas from the cell was absorbed in a dilute milk of lime to produce a bleach liquor. The bleach liquor thus produced amounted to 2.58 volumes for each volume of effluent cell liquor. This bleach liquor was analyzed for available chlorine by addition of KI , acidification with acetic acid, and titration of the liberated iodine with $N/10$ thiosulfate. Each milliliter of the bleach liquor consumed 9.65 ml

of thiosulfate solution. It was analyzed for its total chlorine content by acidification with nitric acid and reduction with nitrous acid, followed by titration of the resulting solution with $N/10$ AgNO_3 . Each milliliter of the bleach liquor consumed 10.85 ml of $N/10$ AgNO_3 , under these conditions. An analysis of the gases leaving the cell and passing to the

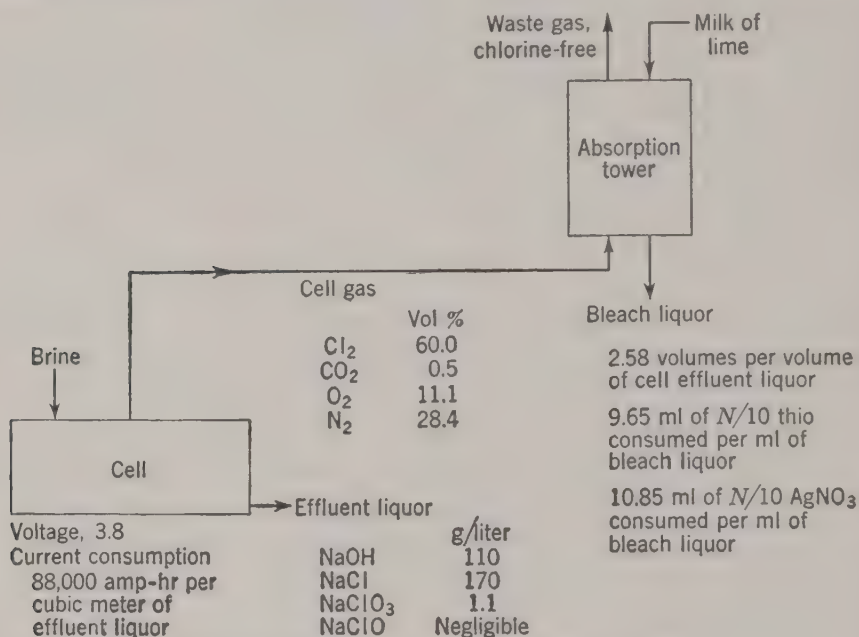


FIG. 9-2. Test data on an Allen-Moore cell.

absorption tower for bleach production showed them to contain 60.0% Cl_2 , 0.5% CO_2 , 11.1% O_2 , and 28.4% N_2 . The gases leaving the bleach absorption tower were chlorine-free.

Calculate

1. The current efficiency of caustic production
2. The current efficiency of chlorine production
3. The current efficiency of hydrogen production

Solution. The principles involved in a material balance on this cell can best be appreciated by reference to Fig. 9-2. Choosing 1 liter of effluent liquor as a convenient basis, the production of caustic is obtained directly from the effluent-liquor analysis and is 110 g. Two methods are available for determining chlorine production. In the first place, it is evident that all chlorine leaving the cell appears in the bleach liquor, and the known amount and total chlorine content of this stream provide a direct measure of the quantity of chlorine manufactured by the cell.¹

¹ The fact that the available chlorine is slightly lower than the total chlorine is typical experience and reflects the occurrence of a certain amount of reduction of the bleach liquor in handling.

A second approach depends upon a sodium balance. In the entering salt, each atom of Na is associated with an atom of Cl. All Na entering in the salt appears in the effluent liquor as NaOH, undecomposed NaCl, or NaClO₃. Each atom of the entering Na that leaves as NaClO₃ or as undecomposed NaCl is still carrying the atom of Cl originally associated with it, but those atoms of Na appearing as NaOH have lost their Cl atoms. The only place the latter could have gone is into the gas, and therefore the atoms of Cl in the gas should equal the mols of NaOH in the effluent liquor. In other words, the current efficiencies of caustic and chlorine production must be equal and can be calculated either from the amount of caustic in the effluent liquor or from the chlorine in the bleach.

In the reasoning of the preceding paragraph, chlorine and sodium balances have been utilized. There remains the possibility of using balances on oxygen and hydrogen. The oxygen picture is complicated slightly by the fact that the gas analysis shows an appreciable amount of N₂, indicating leakage of air into the chlorine-gas line, which is normally operated under a slight suction to prevent any chance of leakage of chlorine outward into the cell room. The gas analysis also shows a small amount of CO₂, which can be ascribed to oxidation of the carbon electrodes. However, the amount of N₂ serves as an index of the quantity of air leakage, and one can subtract the input of O₂ from this source. All the remaining oxygen output as CO₂, O₂, NaOH, and NaClO₃ must have come from decomposition of H₂O in the feed to the cell. The amount of H₂ equivalent to the H₂O decomposed can, therefore, be calculated. A hydrogen balance requires that H₂ in the gas be equal to the H₂O decomposed less H₂ appearing in the effluent liquor as NaOH.

The detailed calculations on a basis of 1 liter of effluent cell liquor appear below.

$110/40 = 2.75$ equivalents of NaOH in cell liquor and of Cl in gas (calculated from the amount of caustic in the effluent liquor)

$2.58(1.085) = 2.80$ equivalents of NaOH in cell liquor and of Cl in gas (calculated from the chlorine in the bleach)

An average of the two methods of determining caustic and chlorine production gives a figure of 2.78 equivalents.

On a basis of 100 mols of gas, the equivalents of Cl equal 120.0, and the atoms of oxygen, exclusive of that from the air, amount to

$$2[0.5 + 11.1 - (21/79)28.4] = 8.1$$

Returning to a basis of 1 liter of effluent liquor, one finds that the atoms of oxygen in the gas, exclusive of that introduced with air, equal

$$2.78(8.1/120.0) = 0.19 \text{ atom}$$

The total oxygen from decomposed H_2O is

$$0.19 + 2.75 + 3(1.1/106) = 2.97 \text{ atoms}$$

From a hydrogen balance, the production of H_2 gas turns out to be $2.97 - (2.75/2) = 1.59$ mols, or 3.18 equivalents.

To summarize, the productions of NaOH , Cl_2 , and H_2 are 2.78, 2.78, and 3.18, respectively, with all quantities expressed as gram equivalents per liter of effluent liquor.

According to the energy relationship discovered by Faraday, a cell reaction consuming 1 g equivalent of each of the reactants and manufacturing 1 g equivalent of each of the products requires 96,500 coulombs of electricity. In this case, the input of electricity is

$$88,000(3600)/1000 = 316,500 \text{ coulombs per liter of effluent liquor}$$

If the cell were 100% efficient (no side reactions), this quantity of electricity ought to yield $316,500/96,500$, or 3.28 equivalents of each product of the reaction $\text{NaCl} + \text{H}_2\text{O} = \text{NaOH} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2$. The actual results are $(2.78/3.28)100 = 85\%$ NaOH and Cl_2 efficiency, and

$$(3.18/3.28)100 = 97\% \text{ H}_2 \text{ efficiency}$$

According to Mantell,¹ the caustic-chlorine current efficiencies of Allen-Moore cells range from 90 to 95%. However, it is likely that these figures represent average plant performance, somewhat lower than that of cells with fresh electrodes and higher than that of cells with worn electrodes, soon to be replaced. The relatively low efficiency of 85% obtained in this case probably means that the test was conducted on a cell that had been on the line for a long time.

Solvay soda. The manufacture of soda ash by the Solvay process is a complicated operation in which good control is absolutely vital to success. Hence, the correct interpretation of data is peculiarly important.

Illustration 3. Certain limited information has been secured concerning the current operation of a Solvay plant, from which it is desired to get as clear a picture as possible of plant performance. The flow sheet of Fig. 9-3 gives the original plant layout and process, but the data indicate that at the present time all the kiln gas going to the carbonating towers flows to the lower of the two towers, which is equivalent to saying that the two carbonating towers are in effect operated as a single unit.

The data available show that the brine fed to the top of the first carbonating tower contains 66 g/liter of CO_2 , 74 of total NH_3 , 4 of fixed NH_3 , and 250 of NaCl . The term "fixed NH_3 " is used to describe the

¹C. L. Mantell, "Industrial Electrochemistry," 3d ed., McGraw-Hill Book Company, Inc., New York, 1950.

ammonia that cannot be evolved from the solution by prolonged boiling. The NaCl is determined analytically by evaporation to dryness, followed by careful low-temperature ignition to constant weight. The analysis of the liquor finally leaving the bottom of the precipitating (carbonating)

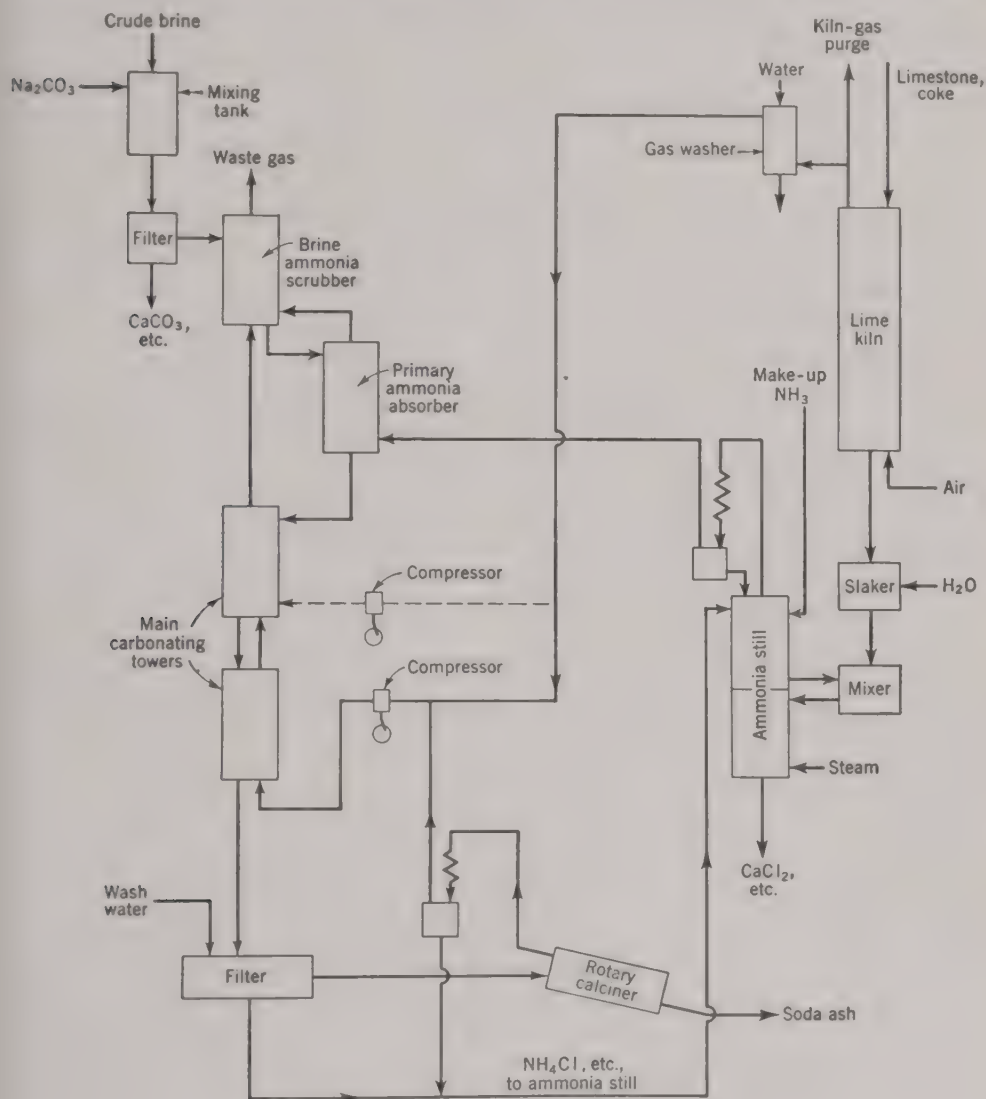


FIG. 9-3. Solvay plant of Illustration 3.

towers averages 39 g/liter of CO_2 , 77 of total NH_3 , 57 of fixed NH_3 , and 85 of NaCl . The mixed gases entering the bottom of the precipitating towers contain approximately 52% of CO_2 , and the final waste gas from the top of the ammonia-recovery system has 6% CO_2 . The plant uses high-grade limestone, low in magnesia. Analyses of the final soda ash produced by the plant show that it averages about 1% salt.

While definite data on the following points are not available, it seems permissible to assume that the limestone decomposition in the kiln averages about 85%, that the hydrogen content of the coke used as fuel may be neglected, that the lime kiln operates with an average of 5% excess air, and that in the washing of the solid bicarbonate about 1% of it is redissolved and goes to the ammonia still with the main filtrate. Calculate

1. The per cent CO_2 in the kiln gas
2. The pounds of coke burnt per 100 lb of CaCO_3 decomposed in the kiln
3. The lime requirement, expressed as mols of CaO produced by the kiln per mol of NaCl in the feed to the plant
4. The gross utilization of NH_3 , expressed as pounds NH_3 added to the brine feed per pound of Na_2CO_3 produced
5. The per cent conversion of NaCl in the feed to Na_2CO_3

Solution. Before starting computations, it is important to be perfectly clear regarding the analytical data. The solution fed to the carbonating tower is made by dissolving CO_2 and NH_3 in a concentrated solution of NaCl . It contains the chlorides, carbonates, carbamates, and bicarbonates of ammonium and sodium, as well as ammonium hydroxide and carbonic acid and presumably ammonia and carbon dioxide as such, all existing in an exceedingly complex equilibrium. Vaporization from this solution would cause loss of ammonia and carbon dioxide, progressively upsetting the equilibrium, but resulting finally in a solution containing nothing but the nonvolatile salts, sodium chloride and ammonium chloride, the latter being the so-called fixed ammonia. This means that any sodium carbonate or bicarbonate existing in the original solution would double-decompose with ammonium chloride to form sodium chloride and the volatile ammonium salts of carbonic acid. It is clear that any solution of pure sodium chloride in water into which ammonia and carbon dioxide are dissolved in any proportions without separation of a third phase would, if boiled long enough, give off all the dissolved constituents and leave behind in the solution the original sodium chloride.

Any further interpretation of the data requires detailed knowledge of the chemistry and mechanism of the steps of the process.

Since the solution entering the top of the precipitating tower contains fixed ammonia, this ammonia must be present as ammonium chloride. Since the original solution contained only sodium chloride, the solution under consideration must contain more equivalents of chlorine than of sodium, *i.e.*, the solution must have lost sodium. Under the circumstances, this can have occurred only by precipitation of NaHCO_3 , the amount of the precipitate being of necessity equivalent to the fixed ammonia left behind in the solution. In other words, as a result of the

process of solution of the ammonia and carbon dioxide, some bicarbonate has already been precipitated from the brine before it enters the main precipitation tower, this bicarbonate presumably being carried in suspension in the liquid.

As the ammoniated brine flows down the precipitation tower, it comes in contact with a counterflowing gas rich in CO_2 . It absorbs this gas, increasing the concentration of ammonium bicarbonate, which, however, immediately double-decomposes with the sodium chloride to form sodium bicarbonate, most of which precipitates. It is clear that all the constituents of the solution are changing except the total ammonia and the chloride. Furthermore, it is improbable that the ammonia is completely constant because it certainly vaporizes to some degree as the ammonia-free gas enters the bottom of the column and it probably continues to vaporize or perhaps condense as the gases go up the column. Clearly, therefore, the chloride content offers the best promise as a basis of computation to enable one to follow the complex changes that are occurring as the brine goes down the tower. In other words, the change in the ratio in the liquid of each constituent to total chloride gives a measure of the gain or loss of that constituent by the liquid stream. The following table shows the analytical data recomputed to this basis. The significance of the results is most easily seen by entering them as shown on the flow sheet of Fig. 9-4.

MATERIAL ENTERING AND LEAVING CARBONATING TOWERS

Basis: 1 atom Cl^- .*

	Entering in liquid stream	Leaving in liquid stream
Total Cl^-	1.0000	1.0000
Total NH_3	0.9655	0.9425
Fixed NH_3	0.0521	0.6978
CO_2	0.3325	0.1844
NaCl	0.9479	0.3022

* This means 1 g atom of Cl in solution as chloride ion, *i.e.*, 1 g ion.

On the basis of this arrangement of the data, a variety of important and interesting relationships comes to light. While it is true that the original data disclose that some chloride goes into the precipitate, this amount is small and may justifiably be ignored for the moment. In the first place, it is seen that the total ammonia leaving the bottom of the tower is in fact less than that entering the top by more than 2%, substantiating the point already made that some vaporization of ammonia does occur. This vaporized ammonia, 0.0230 mol by difference, obviously goes to the ammonia-recovery system, where it is absorbed in the

incoming purified brine. The data also throw quantitative light on the bicarbonate precipitation in the tower. Thus, it is clear that if steady operation of the towers is assumed, *i.e.*, that on the statistical average all the sodium bicarbonate precipitated is carried along with the liquor,

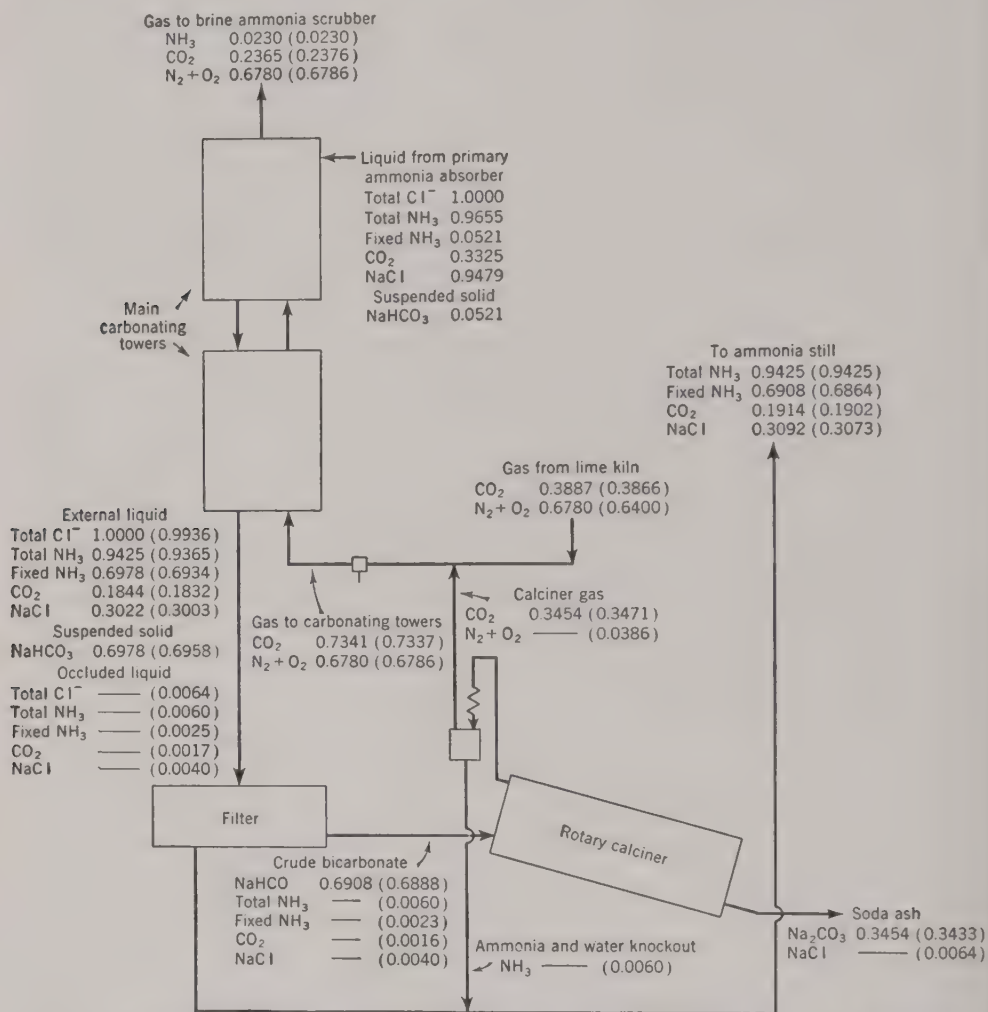


FIG. 9-4. Material balance, uncorrected for occlusion, on Solvay plant of Illustration 3. Basis: 1 equivalent of chlorine. The figures in parentheses are the original values, corrected for the effect of occlusion.

the amount of suspended sodium bicarbonate leaving the bottom of the precipitating tower must be 0.6978 mol per equivalent of chloride constituent, since, as has been explained above, the fixed ammonia in the solution must correspond to the precipitated sodium bicarbonate. Of this, 99%, or 0.6908 mol of solid bicarbonate, goes to the calciner.

Granting no loss of the CO_2 evolved in the calciner, half this, or 0.3454 mol of CO_2 , is fed back to the bottom of the precipitating towers. Moreover, the sodium carbonate product is also equal to 0.3454 mol. All this information comes from component balances on the towers.

1. *The per cent CO_2 in the kiln gas.* In a well-run system of this sort, the still for recovery of ammonia should return substantially all the ammonia and the CO_2 entering it to the ammonia-absorbing towers in the brine-flow system. The reason for this is that the top part of the ammonia still is designed to strip practically all the CO_2 and the free ammonia from the liquor before it goes to the bottom part of the still, since otherwise lime will be wasted in precipitating CO_2 . Moreover, the bottom part of the still should always be operated to secure substantially complete recovery of ammonia. This means that complete recovery, ultimately by solution in the incoming brine, of both the CO_2 and the ammonia contents of the filtrate from the solid bicarbonate can be assumed to take place. Consequently, a CO_2 balance around the whole system exclusive of the lime kiln can be set up. If this is done, it is clear that the only source of CO_2 is from the lime-kiln gases and the only outlets are the 0.3454 mol of CO_2 in the soda ash produced and the waste CO_2 in the top waste gases. Call x the mols of CO_2 entering the tower from the lime kiln and y the mols of nitrogen plus oxygen from the same source. If it is assumed that the inert gases come only from the kiln and use is made of the fact that the ratio of CO_2 to inert gases in the waste gas is 6/94, this is equivalent to writing $x = (6y/94) + 0.3454$. Now attention may be focused on the point of mixing of the kiln and calciner gases. The CO_2 in the mixed gases is $x + 0.3454$ mol. The number of mols of inert gases in the mixture is y . The ratio of CO_2 to inerts in the mixture as shown by analysis is $52/48 = (x + 0.3454)/y$. Solving, $x = 0.3887$ mol CO_2 from the lime kiln and $y = 0.6780$ mol of nitrogen plus oxygen from it. The CO_2 entering the bottom of the tower in the gases is therefore $0.3887 + 0.3454 = 0.7341$ mol. The kiln gas consists of 0.3887 mol CO_2 and 0.6780 mol nitrogen plus oxygen, which gives a composition of 36.5% CO_2 and 63.5% ($\text{N}_2 + \text{O}_2$).

2. *The pounds of coke burnt per 100 lb of CaCO_3 decomposed.*

Basis: 1 mol carbon burnt.

	Mols
O_2 required.....	1
Air required.....	4.76
Air used (5% excess).....	5.00
Products from combustion:	
CO_2	1
$(\text{N}_2 + \text{O}_2)$	4.00

Basis: 100 mols gas produced by lime kiln.

	<i>Mols</i>
(N ₂ + O ₂).....	63.5
CO ₂ , total.....	36.5
CO ₂ from coke, 63.5/4.00.....	15.9
CO ₂ from limestone, 63.5 - 15.9.....	20.6

1 mol of CO₂ from CaCO₃ \approx 1 mol CaCO₃ decomposed = 100 lb CaCO₃ decomposed

$$\frac{\text{lb coke burnt}}{100 \text{ lb CaCO}_3 \text{ decomp.}} = \frac{15.9(12)}{20.6} = 9.27$$

3. *The lime requirement.* On a basis of 1 atom Cl⁻, it was shown that 0.3887 mol CO₂ is required from kiln gas. Of this, 0.3887(20.6/36.5) or 0.220 mol CO₂ is from limestone. On the basis of the reaction



$$\begin{aligned}\text{Mols CaO required} &= 1/2 (\text{mols fixed NH}_3 \text{ leaving system}) \\ &= 1/2 (0.6978) \\ &= 0.3489\end{aligned}$$

The CaO produced for CO₂ requirements = 0.220 mol. Therefore, the lime kiln will be run to satisfy the CaO requirements and will produce excess kiln gases, which will not be sent to the process.

4. *The gross utilization of NH₃.*

Basis: 1 atom Cl⁻.

$$\text{Total NH}_3 \text{ in top of precipitator} = 0.9655 \text{ mol}$$

$$\text{Na}_2\text{CO}_3 \text{ produced} = 0.3454 \text{ mol}$$

$$\text{lb NH}_3/\text{lb Na}_2\text{CO}_3 \text{ produced} = (0.9655)17/(0.3454)106 = 0.448$$

5. *The percentage conversion of NaCl.*

$$\text{Production of Na}_2\text{CO}_3 = 0.3454 \text{ mol}$$

$$\text{NaCl fed in} = 1.000$$

$$\% \text{ conversion} = 2(0.3454)100 = 69.0\%$$

The preceding discussion implicitly assumes purity of the sodium carbonate produced and no contamination of the gases from the bicarbonate calciner. However, the soda ash contains approximately 1% of sodium chloride, and the calciner gases recycled to the precipitating towers after substantially complete removal of water and ammonia contain approximately 10% of air resulting from leakage into the calciner. While these facts are of obviously minor importance in the main analysis of the problem, the situation can well be reexplored in their light.

The mechanism of chloride contamination of the washed bicarbonate crystals is not clear. Sodium chloride might be adsorbed on the surface of the progressively growing crystals of bicarbonate, with no other similar contamination, but this seems unlikely. A more probable explanation is that mother liquor is included or occluded in the crystals as they form and is not completely removed by the washing operation. The performance of the tower will be explored on the basis of this latter assumption.

If occlusion is the major factor, it doubtless occurred progressively during the deposi-

tion of the crystals. This would mean a progressive change in the composition of the occluded liquor. Its composition at the end of the precipitation is known, *i.e.*, that of the effluent liquor from the tower. Its composition at the beginning of precipitation in the primary ammonia absorption unit for ammonia recovery is not known. However, most of the precipitation occurred in the main tower, and one will probably not be far from correct in assuming as the average concentration of the occluded liquor the arithmetic mean of the liquor concentrations at tower entrance and exit, *i.e.*, 0.2585 mol of CO_2 , 0.954 of total NH_3 , 0.625 of NaCl , and 0.375 of fixed NH_3 per mol of chloride constituent.

It is important to keep clearly in mind that there are three separate bodies of material leaving the bottom of the precipitating tower. The first of these is the liquor external to the bicarbonate crystals (the supernatant liquor, if the crystals are allowed to settle), the analysis of which was given in the statement of the problem. The second is the occluded liquor, the composition of which was estimated in the preceding paragraph. The third is the mass of crystals themselves, which are for the moment assumed to be pure bicarbonate. These three bodies and the changes in them must be followed through the operations of filtration, washing, and calcining. For this purpose, one can no longer use the chloride constituent as a direct, unchanging basis, because it is distributed in unknown amount between external and occluded liquor. An algebraic solution will be employed, but the setting up of the equation is somewhat involved. A technique of tabulation will be used which can well be kept in mind for similar cases.

Still using as a basis one equivalent of chloride constituent in the liquor entering the top of the precipitation zone, call y the equivalents of chloride constituent occluded in the crystals as they leave the bottom of the precipitating tower. This leaves $1 - y$ equivalents of chloride constituent in the external liquor itself. Table 9-1 gives in terms of y the quantities of each component in each stream. Columns 1 to 3 refer to the two bodies of liquid leaving the bottom of the tower and should be self-explanatory in the light of the preceding discussion. Column 4 gives the total NaHCO_3 precipitated; this is equal to the fixed NH_3 in the total liquid (see column 3).

It seems reasonable to assume that the volume of liquid occluded per unit of precipitated bicarbonate remains constant throughout the precipitation. As the total volume of liquid per unit of chloride does not change much, the chloride concentration in the tower may be taken as constant. Thus, one can assume that the ratio in the precipitate of total chloride constituent to solid bicarbonate remains constant throughout the precipitation process. One also assumes that the occluded liquor removed by washing has substantially the same composition as the external liquor leaving the bottom of the tower. With these two assumptions one can calculate the reduction of occlusions by washing as in column 5. The result should be fairly satisfactory because it is used only to estimate a fairly minor correction term, *i.e.*, the fraction of the constituents in the occluded liquor that is removed in the wash water along with the 1% of the bicarbonate dissolved in the washing operation.

The occlusions left after washing (column 6) will be equal to the original occluded liquid (column 2) less that lost by washing (column 5). Notice that the NaHCO_3 that is dissolved upon washing is also included in column 5 and that remaining is shown in column 6.

Column 7 gives the quantities in the main filtrate plus wash water as obtained by addition of 1 and 5 (or the difference of 3 and 6). Here the NaHCO_3 is measured as such. Column 8 transforms the figures of column 7 into the same convention of reporting analytical results used throughout the problem by reporting the sodium in the NaHCO_3 as NaCl and the carbonate as CO_2 . This is done because the NaHCO_3 is in the filtrate plus wash not as solid bicarbonate but as Na^+ , H^+ , and CO_3^- ions.

TABLE 9-1. ANALYSIS OF SOLVAY PROCESS CONDITIONS

Basis: 1 equivalent of total chloride constituent in the initial brine.

Constituent	(1) In external liquid	(2) In occluded liquid	(3) In total liquid (1) + (2)	(4) As solid precipitate	(5) Reduction of occlusions by washing	(6) Occlusions left after washing (2) - (5)	(7) In filtrate plus wash water (1 + 5) or (3) - (6)	(8) In filtrate plus wash water (NaHCO ₃ reported as NaCl + CO ₂)
Cl ⁻	1 - y	y	1	0.01y	0.99y	1 - 0.99y	1 - 0.99y
CO ₂	0.1844(1 - y)	0.2585y	0.1844 + 0.074y	0.01y(0.1844)	0.2567y	0.1844 - 0.183y	0.1914 - 0.186y
Total NH ₃	0.9425(1 - y)	0.9540y	0.9425 + 0.0115y	0.01y(0.9425)	0.9446y	0.9425 - 0.933y	0.9425 - 0.933y
Fixed NH ₃	0.6978(1 - y)	0.375y	0.6978 - 0.3228y	0.01y(0.6978)	0.368y	0.6978 - 0.691y	0.6908 - 0.688y
NaCl.....	0.3022(1 - y)	0.625y	0.3022 + 0.3228y	0.01y(0.3022)	0.622y	0.3022 - 0.299y	0.3092 - 0.302y
NaHCO ₃	0.6978 - 0.3228y	0.01(0.6978 - 0.3228y)	0.6908 - 0.3196y	0.0070 - 0.0032y

In calcination the occluded fixed ammonia reacts with solid bicarbonate, forming volatile $(\text{NH}_4)_2\text{CO}_3$ and correspondingly reducing the amount of the latter and increasing the sodium chloride. The amount of sodium bicarbonate that goes to carbonate on calcination will be equal to the sodium bicarbonate left after washing ($0.6908 - 0.3196y$), less the occluded NH_3 ($0.368y$). The sodium carbonate formed will of course be equal to one-half this amount. Since the weight ratio of salt to carbonate in the final product is $1/99$, one can write

$$\frac{0.99y(58.45)(2)}{106(0.6908 - 0.3196y - 0.368y)} = \frac{1}{99}$$

whence $y = 0.0064$.

This gives 0.9936 atom Cl^- in external liquid. The amounts of the other constituents in the external liquid have been calculated. From column 6 one obtains the occlusions with the precipitated bicarbonate and also those in the filtrate that goes to the ammonia still.

The quantities of interest in the table have been evaluated and inserted in parentheses in the flow sheet of Fig. 9-4.* The changes are not large enough to modify the general picture of the operation as drawn from the first interpretation, but proper corrections of this sort are clearly necessary for any dependable analysis of the relationships, such as is necessary when the presence of impurities in the product affects the economics of the process.

It will be noted that these conclusions are independent of the technique of operation of the calciner, provided only that it recovers all the volatilizable constituents of the bicarbonate fed to it.

With the new corrected values obtained for the various streams several quantities may now be calculated more accurately than could be done previously.

1. *The per cent CO_2 in the kiln gas.* The kiln gas contains 0.3866 mol CO_2 and 0.6400 ($\text{N}_2 + \text{O}_2$), which is equivalent to 37.8% CO_2 and 62.2% ($\text{N}_2 + \text{O}_2$). Without correcting for occlusion, a composition of 36.5% CO_2 and 63.5% ($\text{N}_2 + \text{O}_2$) was obtained.

2. *The pounds of coke burnt per 100 lb CaCO_3 decomposed.*

Basis: 1 mol carbon burnt.

	Mols
O_2 required.....	1
Air required.....	4.76
Air used (5% excess).....	5.00
Products from combustion:	
CO_2	1
$(\text{N}_2 + \text{O}_2)$	4.00

* With regard to the figures in parentheses, the method of calculation obviously implies a correction to the figures on the liquor entering the precipitation tower, on account of the accompanying bicarbonate. Thus, approximately 0.05% of the total chloride constituent is occluded before entering the precipitation tower. However, while the occluded components are not negligible relative to the totals, the sum of external and occluded components per equivalent of total chloride (also external plus occluded) does not differ within the fourth significant figure from the figures given in the flow sheet for the original case. Hence in the flow sheet no changes are shown for these figures, but it must be kept in mind that as applied to the case in which occlusion is assumed these figures refer, not to external liquid alone, but to the sum of external and occluded portions.

Basis: 100 mols kiln gas.

	Mols
(N ₂ + O ₂).....	62.2
CO ₂ , total.....	37.8
CO ₂ from coke, 62.2/4.00.....	15.6
CO ₂ from limestone.....	22.2

1 mol of CO₂ from CaCO₃ \approx 1 mol CaCO₃ decomposed = 100 lb CaCO₃ decomposed
 lb coke burnt per 100 lb CaCO₃ decomposed = 15.6(12)/22.2
 = 8.43 (uncorrected value was 9.27)

3. The lime requirement.

Basis: 1 atom Cl⁻ entering precipitating tower.

CO₂ from kiln gas = 0.3866 mol

CO₂ from limestone = 0.3866(22.2/37.8) = 0.227 mol

On the basis of 2NH₄Cl + CaO = 2NH₃ + CaCl₂ + H₂O,

Mols CaO required = 1/2 (mols fixed NH₃ leaving system)

= 1/2 (0.6864)

= 0.3432 mol (uncorrected value was 0.3489)

4. The gross utilization of NH₃.

Basis: 1 atom Cl⁻ entering precipitating tower.

Total NH₃ in top of precipitator = 0.9655 mol

NaHCO₃ entering calciner, 0.6908 - 0.3196(0.0064) = 0.6888 mol

NaHCO₃ lost by conversion to NaCl = 0.368(0.0064) = 0.0023 mol

Na₂CO₃ produced = 0.6865/2 = 0.3433 mol

lb NH₃/lb Na₂CO₃ produced = 0.9655(17)/0.3433(106)

= 0.451 (uncorrected value was 0.448)

5. The percentage conversion of NaCl.

Na₂CO₃ produced = 0.3433 mol NaCl fed in = 1.0000 mol

% conversion: 2(0.3433)100 = 68.6 (uncorrected value was 69.0)

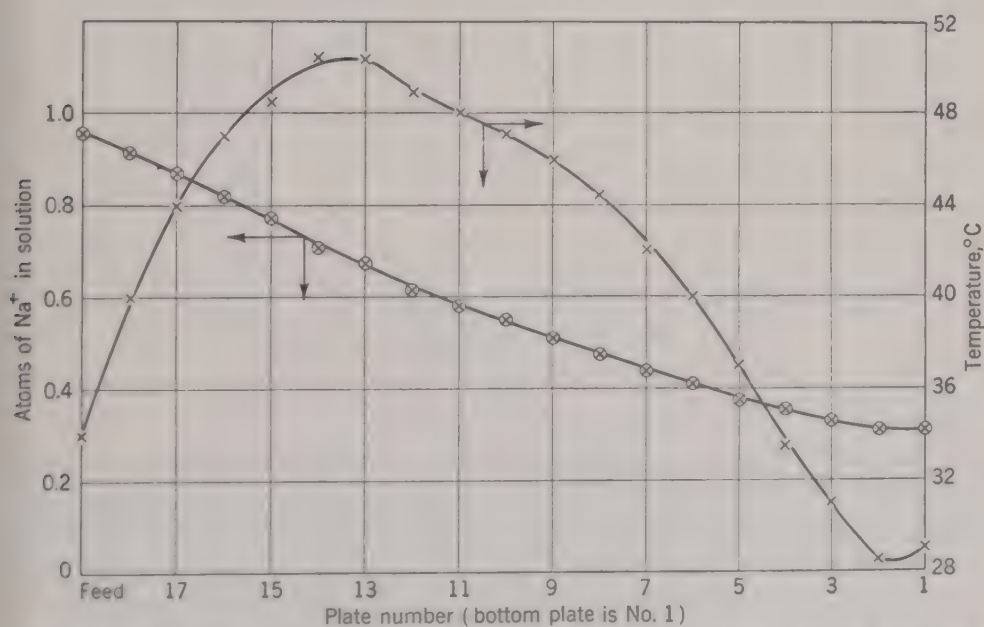
Illustration 4. The data of Table 9-2 on the operation of an 18-plate Solvay tower, 70 ft high and 6½ ft in diameter, were published by Bradburn.¹ The analyses are of the feed to the top of the column and of the liquid flowing out of each plate. The tower produced 44 tons per 24-hr day of soda ash from the calciner. Gas from the lime kiln averaged 36% CO₂, 1.6% O₂, and 62.4% N₂, while that from the calciner was 84% CO₂. The mixed gas contained 45% CO₂, was fed to the bottom of the column under a pressure of 55 in. Hg, and left the top at 9 in. The slurry leaving the bottom of the column had a specific gravity of 1.19, a figure that did not change much in the flow through the column, owing to the compensating effects of the density of the precipitated bicarbonate and of the change in volume of the residual mother liquor.

In the table the figures for the free and total ammonia are reported as titer, *i.e.*, the milliliters of *N*/20 solution used in titrating 1 ml of the solution being analyzed.

¹ J. A. Bradburn, *Z. angew. Chem.*, p. 78 (1898).

TABLE 9-2. OPERATING DATA ON 18-PLATE SOLVAY TOWER

Plate No.	Temp., °C	Free NH_3 (titer)	Total NH_3 (titer)	NaCl , g/liter	CO_2 , g/liter
Feed	34	85	89	248.8	67
18	40	81.2	89.2	242.4	77.2
17	44	77.4	89	231	76
16	47	71.4	88.3	221	73.3
15	48.5	66	88.6	210	69.1
14	50.5	62.5	89	191	65.5
13	50.5	58.2	89	188.2	63
12	49	53	89.3	170	59.3
11	48	50	89.2	162.2	57
10	47	46.8	89	150.6	54
9	46	44	89	139.4	52
8	44.5	40	89	131	49
7	42	36.5	89.2	123	47.1
6	40	33.3	89.6	115	45
5	37	30	89.6	105.8	43.3
4	33.5	27	89.3	99.7	41.8
3	31	24.7	89.8	94	40.6
2	28.5	23	90	88	40
1	29	23	89.8	88.3	40

FIG. 9-5. Bradburn data. Sodium in solution vs. plate number. Basis: 1 atom of total Cl^- .

These data can be analyzed by the method of Illustration 3. The results can be plotted in different ways. Figure 9-5 shows the atomic ratio of sodium to chlorine in the solution, plotted against the plate number in the column. The temperature data are shown on the same figure. The sodium curve is smooth and consistent, showing a reasonably uniform rate of precipitation of bicarbonate per plate until one approaches

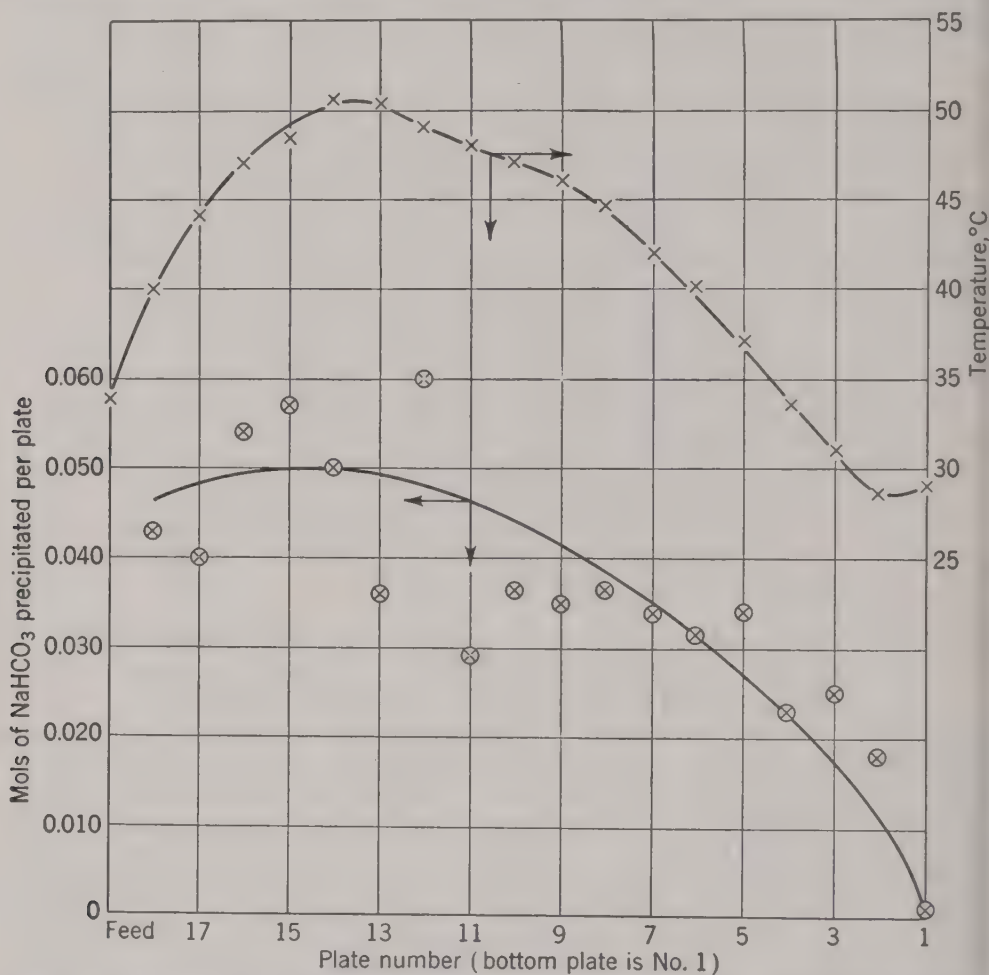


FIG. 9-6. Bradburn data. Sodium bicarbonate precipitated per plate vs. plate number. Basis: 1 atom of total Cl^- .

the bottom of the column, where the rate drops off, precipitation ceasing below the second plate. However, one can plot sodium precipitated per plate against plate number as in Fig. 9-6. Despite the fact that they are the same data, the points *look* far less consistent. The obvious reason is that the ordinates for Fig. 9-6 are small differences between relatively large numbers, extremely sensitive to small fractional errors in the original data. Nevertheless, Fig. 9-6 is the more informative of the two.

It indicates a definite increase in precipitation rate in the upper plates of the tower, which can easily escape notice from inspection of Fig. 9-5. Moreover, it brings out wide fluctuations on plates 11, 12, and 13. One would at first be inclined to ascribe these to experimental errors in analysis, except for the fact that this region also shows abnormality in the temperature curves. The slow precipitation, particularly in the lower part of the tower, is due to the necessity for building up crystals of bicarbonate of relatively uniform particle size, so as to get good filtration characteristics, *i.e.*, high filtration rates and low liquid retention. By maintaining a low degree of supersaturation during the later stages of precipitation, the crystals already formed can be allowed to grow without running the risk of developing new crystal nuclei, which would inevitably result in the presence of relatively large numbers of small crystals along with the large ones in the final suspension.

The way in which a given set of data are presented can be extremely important in bringing out their significance and arriving at a sound interpretation.

Illustration 5. Hempel and Tedesco¹ published the data of the adjoining table, obtained by introducing pure CO₂ gas at a gauge pressure of 1.8 atm into various solutions of salt in aqueous ammonia. The magma was agitated until substantial equilibrium was secured, the remaining liquor was filtered off, and the precipitate was washed free of mother liquor by using as wash water a solution of sodium bicarbonate saturated at 30°C. The resulting precipitate was weighed and analyzed.

Basis: 1000 ml of initial solution.

Weight in initial solution, g		Weight of precipitate, g	
NH ₃	NaCl	NaHCO ₃	NH ₄ HCO ₃
76.52	262.22	269.46	11.06
82.86	257.86	282.08	11.46
133.27	222.56	261.34	83.50
210.31	194.98	248.5	565.30

The first two vertical columns give the concentrations in the initial solutions of salt in ammonia liquor, before the introduction of CO₂, and the last two give the weights of each of the two bicarbonates in the precipitates produced. These well-washed precipitates were substantially free of chlorides.² The table below converts the figures to mols.

¹ W. Hempel and H. Tedesco, *Z. angew. Chem.*, **24**, 2459 (1911).

² This fact supports the assumption made on p. 303 that residual chlorides in the washed precipitate are due to mother liquor entrapped in the crystal magma, which

Basis: 1000 ml of initial solution.

Mols in initial solution		Mols precipitated		Per cent NaCl converted
NH ₃	NaCl	NaHCO ₃	NH ₄ HCO ₃	
4.50	4.45	3.21	0.140	72
4.86	4.41	3.36	0.145	76
7.84	3.81	3.11	1.056	82
12.37	3.34	2.96	7.16	89

Inspection of the data makes it clear that, as the ammonia content of the initial solution rises much above 80 g/liter, there is a sudden increase in ammonium bicarbonate coprecipitating with the sodium salt. It is true that there is some ammonium bicarbonate in the precipitate at initial ammonia concentrations below the level stated. However, this ammonium bicarbonate precipitating at low concentrations is only about 4 per cent of the sodium bicarbonate and apparently increases quite slowly as the ammonia concentration rises, until the latter is somewhat more than 80 g/liter. It looks as though these lower values of ammonium bicarbonate contamination represent not precipitated salt but rather some form of superficial contamination.¹ This small contamination is not serious, but the gross precipitation of ammonium bicarbonate at the high ammonia concentrations is obviously to be avoided, since, while it could be removed in the calcining operation, its bulk is so great that it would seriously interfere with filtration and washing and probably increase the ammonia losses in calcining. Is there any possibility of securing the high salt conversions of the last runs without the corresponding ammonium bicarbonate contamination of the precipitate?

Hempel and Tedesco were convinced that carbonation went substantially to completion in each of their experiments. If this be true, it means that the mother liquor left in the last experiments must be in equilibrium with both bicarbonates. Now in true heterogeneous equilibrium the compositions of the phases are independent of the quantity of the phases. Thus, in the last two runs if one could remove the precipitated ammonium salt, one would in no way affect the composition or amount of the liquid or of the solid sodium bicarbonate. Similarly, if one could adjust the conditions of the operation so as to avoid formation of the solid NH₄HCO₃, this might be done without in any way affecting

was not completely removed by washing in the commercial operation. It indicates that this entrained mother liquor was held between the crystal grains and not occluded within them, since otherwise a washing operation which dissolved practically none of the bicarbonate could not eliminate the chlorides.

¹ For example, it might be a limited solubility of the ammonium bicarbonate in the sodium salt in solid solution.

the quantities or compositions of the other phases. Theoretically this can be achieved by stoichiometric control of the operation, *i.e.*, by seeing to it that, without affecting the other quantities, the material for the formation of the solid ammonium bicarbonate is not introduced. This solid is made up of three components, ammonia, water, and carbon dioxide. The quantity of CO_2 to be introduced in this type of operation is not under the control of the operator, because enough must be admitted to keep the pressure up to 1.8 atm, however much this amount of CO_2 may be. The quantity of both the other components, ammonia and water, can, however, be reduced by an amount equal to the ammonium bicarbonate which it is desired *not to form*. This should result in the setting up of exactly the same equilibrium, so far as the compositions and quantities of the liquid and sodium bicarbonate phases are concerned. In the light of the first two runs it appears that one must anticipate a contamination of the sodium bicarbonate precipitate with approximately 4% of the ammonium salt, corresponding to about 10.4 g NH_4HCO_3 in the third run and 9.9 g in the fourth. This would result in eliminating the formation of $83.5 - 10.4$ or 73.1 g of ammonium bicarbonate in the third run and $565.3 - 9.9 = 555.4$ g in the fourth run. Hence, if under the conditions of the fourth run, one will start with an initial solution containing $12.37 - 7.03 = 5.34$ mols of ammonia and 7.03 less mols of water than was actually employed, using the same quantity of initial salt, one should wind up with the same quantity of sodium bicarbonate and the same mother liquor, but with only 9.9 g of ammonium bicarbonate. One would thus secure the high salt conversion of the last run and at the same time eliminate the excessive contamination of the precipitate with ammonium bicarbonate.

The trouble with this operation is that the quantity of strong ammonia solution required is insufficient to dissolve the salt. One could introduce the salt and let the excess stay in suspension in the liquid. However, while theoretically this salt should ultimately dissolve and yield the desired final equilibrium, the salt crystals left suspended in the original ammonia solution before carbonation starts become coated with precipitated bicarbonate, and their rate of solution, as salt is consumed by the chemical reaction of carbonation, is so retarded that the operation is completely impractical. On the other hand, it is by no means out of the question to introduce the solution saturated with salt into the top of the carbonating tower, let precipitation go on to substantial completion at the carbon-dioxide pressure existing in the tower, and then remove the solution and resaturate it with salt, reintroducing it into the tower and allowing the carbonation reaction to proceed. Whether resaturation is justified or not depends upon the economic importance, for any particular plant, of high efficiency in the utilization of salt.

A much clearer picture of what was going on in Hempel and Tedesco's experiments is obtained by use of a Janecke diagram.¹ Take as a basis 1 mol of mixture of any neutral salts having only two anions and two cations between them (in this case, NaCl and NH_4HCO_3). Construct a plot such as Fig. 9-7, in which the abscissas are the mols of sodium ion

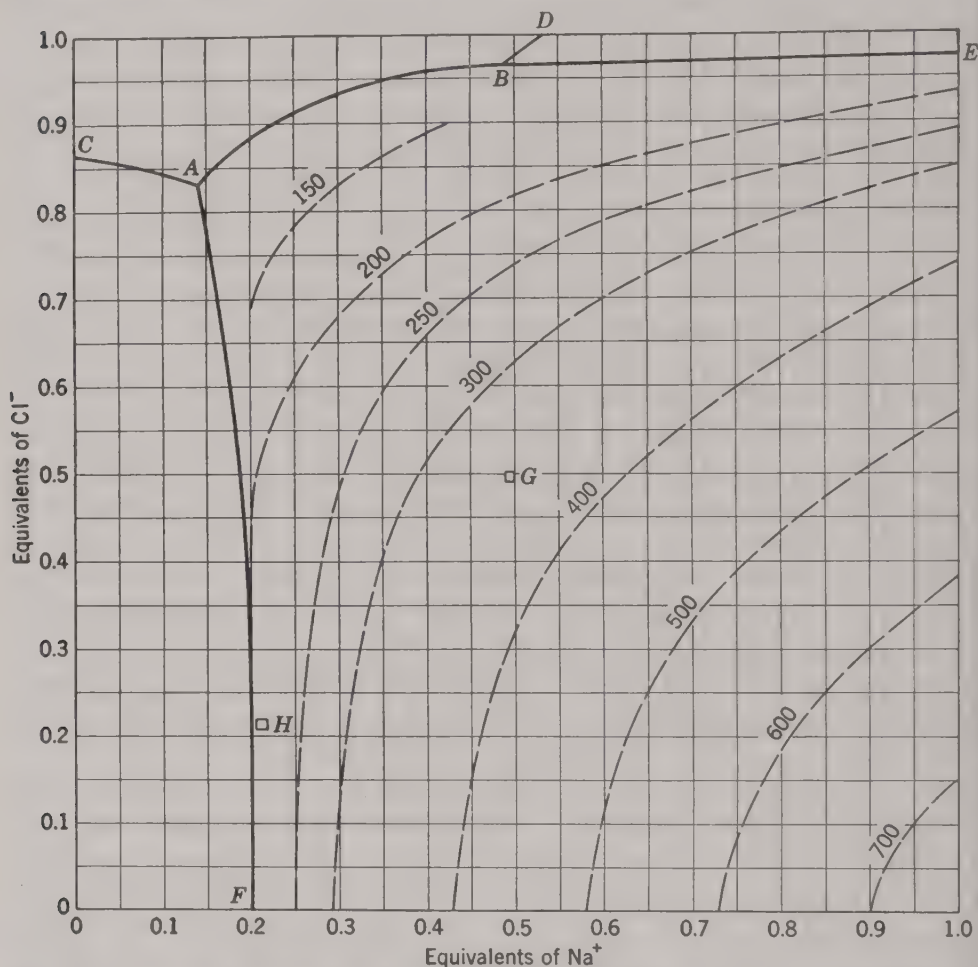


FIG. 9-7. Janecke diagram for solutions containing Na^+ , NH_4^+ , Cl^- , and HCO_3^- at 30°C . Basis: 1 equivalent of Na^+ plus NH_4^+ . The numbers on the dotted lines indicate grams of water at saturation with NaHCO_3 .

and the ordinates those of chlorine ion. Obviously, the mols of ammonium ion may be read from right to left and those of bicarbonate from top to bottom; *i.e.*, each point in the square corresponds to a single specific salt mixture. Any solution of these salts corresponds to such a unique point. Furthermore, if any neutral salt that is a combination of the ions present be either added to the solution or taken from it (as

¹ E. Janecke, *Z. anorg. Chem.*, **51**, 132 (1906); *Z. angew. Chem.*, **20**, 1559 (1907).

by crystallization), the solution changes composition along a straight line through the point corresponding to its initial composition and the point representing the composition of the salt added or separated.¹

Such a solution has five phase-rule components, corresponding to the four ions and the solvent, and if one grants the presence of liquid and gaseous phases, its variance is five. However, it presumes that the sum of anions and cations is the same (neutral salts); this intensive restriction reduces the variance to four. The diagram is normally used for an isothermal system, so that, in the absence of solid phases, the degrees of freedom are three and each solid in equilibrium with the solution reduces them by one. Hence, equilibrium coexistence of three solid phases means a nonvariant system, corresponding to a fixed point on the diagram. Two solids give monovariance, corresponding to a line, since if the abscissa is given, the ordinate is thereby fixed. However, a single solid can be represented by any point that lies within the area of potential existence of that solid.

The quantitative details of the diagram can be determined only by experimental data on the system in question. Figure 9-7 is based on laboratory measurements at 30°C.* *A* is the nonvariant point corresponding to coexistence of solid NH_4Cl and the two bicarbonates; *B* corresponds to the two chlorides and NaHCO_3 . Along *AC* the two ammonium salts can coexist; along *BD*, the two chlorides; along *BE*, the two sodium salts; along *AF*, the two bicarbonates; and along *AB*, NH_4Cl and NaHCO_3 . Thus far, the plot gives information regarding the salts only. Its axes are not designed to tell anything of absolute concentrations, *i.e.*, about the amount of solvent present. However, if at any specific point in an area, such as that between the lower right corner and the curve *FABE*, solid (NaHCO_3) be present in equilibrium, the fact that ordinate and abscissa, both intensive variables, are specified by the location of the point means that all other intensive properties of the system, including concentration of the solution, are also fixed. In other words, in the area one can draw curves of constant concentration; these are shown dotted and are expressed as grams of water at saturation per mol of salt mixture in the solution. Unfortunately, in the given diagram the dotted curves have had to be estimated because of paucity of data.

More disturbing than this, however, study of these data convinces one that they are in serious error in that the sum of anions in the solutions analyzed is far less than that of the cations; *i.e.*, there is not in fact enough CO_2 in solution to convert alkali in excess of chloride to bicarbonate (*e.g.*, contrast these data with the analyses of the liquor on the

¹ See also the discussion of phase diagrams in Chap. 11.

* P. P. Fedotieff, *Z. angew. Chem.*, **17**, 1653 (1904); B. Neumann and R. Domke, *Z. Elektrochem.*, **34**, 136 (1928).

two bottom plates of the tower of Illustration 4, which are clearly in substantial equilibrium with incoming gas). Most if not all the laboratory workers *assumed* all titratable alkali to be bicarbonate. In view of the weakness of ammonia as a base and particularly of carbon dioxide as an acid, together with the low solubility of the latter, a molal ratio of unity of total CO_2 to free ammonia in solution is unthinkable, and in fact the ratio is far less. In other words, the assumption of "neutrality" of the dissolved salts, which is the normal basis for use of the Janecke diagram, is unjustified.

On the other hand, study of the situation shows that it is not too black. Solution neutrality fixes one phase-rule variable. All the laboratory investigators, however, worked at constant (or substantially constant) CO_2 pressure, which itself is a phase-rule variable. This being the case, lack of "neutrality" of the solution does not increase the degrees of freedom of the system, because for it is substituted constancy of pressure. One must, however, make sure that the method of plotting is still legitimate. If one will use as a basis one equivalent of total sodium plus total ammonia in the solution and will interpret the abscissa as the ratio of equivalents of sodium to total equivalents of sodium plus ammonia, and the ordinates solely as the ratio of equivalents of chlorine to sodium plus ammonia, the situation becomes clear. What one must not do is to interpret the vertical distance down from the top of the plot as bicarbonate constituent. The dependability of the nonvariant points *A* and *B* and of the two-solid-phase lines is unimpaired,¹ but the uncertainty of the dotted water lines is enhanced (except on the right-hand edge) by the error in CO_2 .

The significance of the table on page 310 now becomes clear. For the first run the abscissa at the start is 0.497 and the ordinate obviously the same. Getting the composition of the mother liquor from the table by difference, one finds that the abscissa is 0.222 and the chloride ordinate 0.795. Plotting the first point *G*, drawing a line through it from the NaHCO_3 corner of the diagram, and extending it to the abscissa 0.222 gives a chloride ordinate of 0.774. The check is good, and it is obvious that the solution never got out of the area in which NaHCO_3 is the only possible equilibrium solid phase. Treating the fourth run similarly gives a starting point *H* of 0.212, 0.212, through which the NaHCO_3 precipitation line almost immediately hits line *FA* where coprecipitation of NH_4HCO_3 starts. Solution concentration then travels along *FA* toward *A*. However, calculation from the table of the diagram coordinates of the mother liquor by difference gives an abscissa 0.068 and ordinate 0.597. The lowest attainable abscissa according to Fig. 9-7 is 0.14 at point *A* with an ordinate of 0.83. The discrepancy between the two

¹ As is to be expected, liquid composition is very insensitive to CO_2 pressure.

pairs of figures is due to the fact that, in washing a precipitate so rich in NH_4HCO_3 with a saturated solution of NaHCO_3 , a considerable amount of the former dissolved. The composition of the mother liquor calculated by difference is therefore high in ammonia, lowering the computed value of both ordinate and abscissa.

Had Hempel and Tedesco planned their work on the basis of a careful analysis of the physical chemical information available to them, or even interpreted their results in that light, they could not have failed to make their work far more constructive.

Illustration 6. A Southern paper mill is engaged in the manufacture of pulp by the sulfate process. A flow sheet of the plant is shown in Fig. 9-8. Note that in this particular mill the supply of make-up alkali and sulfur, which the process requires, is being purchased in the form of salt cake and elemental sulfur.

Table 9-3 gives actual operating data, taken from the plant records of this mill. The figures represent the average performance for 24 hr of operation, during a period when the plant was running smoothly and performance was typical of normal conditions.

TABLE 9-3. CHEMICALS USED IN SULFATE PROCESS

Quantities per ton of pulp:

Salt cake.....	196.2 lb
Sulfur.....	14.7 lb
Fresh lime (as active CaO).....	35.6 lb
Reburnt lime (as active CaO).....	359.1 lb
White liquor.....	77.9 cu ft

White-liquor analysis (all substances expressed as equivalents of alkali):

	<i>G eq/liter</i>
Active alkali, $\text{NaOH} + \text{Na}_2\text{S}$	3.48
Sulfidity, $\text{Na}_2\text{S}/(\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3)$	0.235
Activity, $(\text{NaOH} + \text{Na}_2\text{S})/(\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3)$	0.805
Reduction, $\text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$	0.937

Lime analysis:

	<i>Weight %</i>
Active CaO in unslaked fresh make-up lime.....	90.5
Active CaO in unburnt lime.....	81.4
Free CaO in lime sludge.....	1.1
Total alkali in lime sludge (as per cent Na_2SO_4).....	4.3
Residual solids in lime sludge.....	48.5

The alkali in the lime sludge was determined by washing it thoroughly with dilute $(\text{NH}_4)_2\text{CO}_3$ solution, filtering, adding excess H_2SO_4 to the filtrate, evaporating, igniting, and weighing the residue. The result is reported as weight of Na_2SO_4 obtained per 100 parts of sample. The insoluble residue from the filtration was dried, weighed, and reported as the residual solids in the lime sludge.

The pulp was washed twice and after washing was essentially sodium-

and sulfur-free. The first wash water was added to the black liquor. The second wash water, containing sodium in an amount calculated as 21.7 lb of Na_2O^* per ton of pulp, was too dilute for economical recovery and was discarded.

From the data of Falk, quoted by Schorger,¹ it is estimated that the relief condensate (oil and water) contains about 1.7 lb of sulfur per ton of

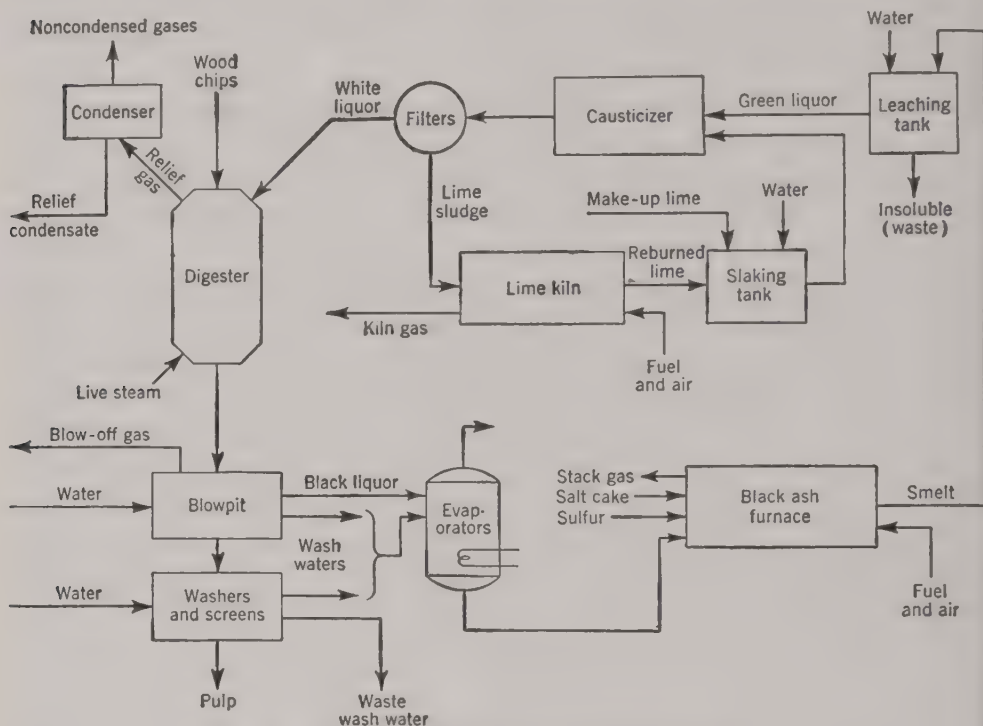


FIG. 9-8. Sulfate pulp mill of Illustration 6.

pulp. According to Schorger, the sulfur content of the noncondensed gases is of the order of 0.02 lb per ton of pulp.

This plant has just been acquired by a large paper company operating a chain of mills. As an engineer employed by the new owner, you have been asked to analyze the above information and present your comments. What points would you stress in your report?

Discussion. An analysis of the data ought to throw light on how the chemicals are being consumed and should suggest methods for improving economy in their utilization. The major chemical costs are the salt cake and the sulfur, compared to which lime is relatively cheap. Hence,

* It is customary in the trade to express the strength of solid caustic soda and of its solutions as per cent Na_2O .

¹ A. W. Schorger, "The Chemistry of Cellulose and Wood," McGraw-Hill Book Company, Inc., New York, 1926.

attention should be focused primarily on the losses of sodium and sulfur at various points in the system.

Let the basis of computation be a ton of pulp, and express the quantities of sodium and sulfur at various points in terms of pound atoms. From the figures on input, the sodium supplied to the plant as salt cake (which can be considered as being practically all Na_2SO_4) amounts to

$$196.2(2)/142 = 2.77 \text{ atoms}$$

The sulfur introduced in the salt cake and as elemental sulfur is

$$(196.2/142) + (14.7/32) = 1.84 \text{ atoms}$$

Attention may be centered first of all upon the losses of sodium. Consideration of the flow sheet will show that there are three places where major losses of sodium can be expected: (1) the waste wash water; (2) volatile material and entrained solids in the stack gases from the burner; and (3) mechanical losses in the lime-recovery system, *i.e.*, handling losses and entrainment of solids in the kiln gases. Sodium losses in the pulp, the blowoff gas, the insoluble residue after leaching, and elsewhere in the system ought to be negligible.

The loss in the waste wash water has been measured directly and is equal to $21.7(2)/62 = 0.70$ atom, or about a quarter of the total. Three-quarters of the sodium consumption must be accounted for by 2 and 3.

No information is available on losses from the burner, but losses during recovery of the lime can be estimated from the amount of make-up lime required. If the losses of sodium and calcium all occur during handling of the sludge or as entrainment of dust in the kiln gases, then the sodium and calcium must be lost in the same ratio as that in which they exist in the sludge entering the kiln. From the known amount of calcium loss, *i.e.*, the make-up required, and the ratio of sodium to calcium in the sludge, one can estimate the absolute amount of sodium loss.

Although the principle of the calculation is essentially that outlined in the preceding paragraph, a slight modification is required by the fact that the analysis of the sludge is not complete, and one cannot distinguish between CaCO_3 and inerts in the residual solids. The method of analysis is such that the so-called residual solids represent the weight of inerts in the sludge plus the calcium in the form of CaCO_3 ; and this suggests that instead of using Ca as a "tracer" for losses of Na, it is better to use the sum of the inerts and Ca, the latter being expressed as CaCO_3 . The make-up to the lime-recovery system is

$$35.6(100/56) + 35.6(100 - 90.5)/90.5 = 67.2 \text{ lb}$$

of inerts plus Ca as CaCO_3 . In the sludge, the ratio of Na to inerts plus Ca, as CaCO_3 , equals $4.3(2)/(142)(48.5) = 0.00125$ atom of Na

per lb; and the estimated loss of Na from the lime-recovery system is $0.00125(67.2) = 0.08$ atom, or about 3% of total Na losses from the plant. By difference, it is seen that losses of Na in the burner must amount to $2.77 - 0.70 - 0.08 = 1.99$ atoms, or almost three-quarters of all losses of this element.

The make-up sulfur introduced as Na_2SO_4 and S was 1.84 atoms, as noted above. The proportion of this sulfur leaving as mercaptans and sulfides in the relief condensate and noncondensed gases has been estimated as equal to $(1.70 + 0.02)/32 = 0.05$ atom, less than 3% of the total. Evidently, the chief losses are elsewhere. Referring to the flow sheet, one concludes that the chief losses of sulfur must be in (1) the waste wash water, (2) volatile compounds and entrained solids in the burner-stack gases, and (3) entrained solids in the lime-kiln gases.

While no direct determination was made of sulfur in the waste wash water, the sodium content is reported, and it is reasonable to suppose that the ratio of sulfur to sodium is practically the same in the waste wash water as it is in the mixture of pulp and spent liquor discharged from the bottom of the digesters. The only possibility that might interfere with this conclusion is that sodium and sulfur compounds may have been adsorbed to some extent on the pulp in the digester, and then, when removed by washing, they may have been removed at different rates, thus appearing in different ratios as the washing progressed. However, by far the greater part of the sodium and sulfur leaving the digester must have been in solution, and the amount in adsorbed form was in all probability too small to have any significant effect.

In order to calculate the ratio of Na to S in the mixture discharged from the bottom of the digesters, the amounts of Na and S supplied to the digesters in the white liquor are first obtained and the sulfur is then corrected for that evolved in the blowoff gas. Let the gram equivalents of NaOH, Na_2S , Na_2CO_3 , and Na_2SO_4 per liter of white liquor be x , y , z , and u , respectively. From the analysis, one can set up the following equations:

$$\begin{aligned}x + y &= 3.48 \\y/(x + y + z) &= 0.235 \\(x + y)/(x + y + z) &= 0.805 \\y/(y + u) &= 0.937\end{aligned}$$

Solving, $x = 2.46$, $y = 1.02$, $z = 0.84$, and $u = 0.07$. Per liter of white liquor, the gram equivalents of Na amount to

$$2.46 + 1.02 + 0.84 + 0.07 = 4.39$$

while the atoms of sulfur total $0.5(1.02 + 0.07) = 0.55$.

On a basis of 1 ton of pulp, the corresponding quantities are

$$77.9(28.3)(4.39)/454 = 21.3 \text{ pound atoms of Na}$$

and $77.9(28.3)(0.55)/454 = 2.67$ pound atoms of S. Subtraction of 0.05 atom of S in the blowoff gas gives 2.62 atoms in the mixture of pulp and liquor discharged from the bottom of the digesters. The S/Na ratio in this stream is therefore equal to 2.62/21.3, or 0.123. The resultant estimate of sulfur loss in waste wash water is

$$0.123(0.70) = 0.09 \text{ atom of S}$$

This amounts to approximately 5% of the total sulfur make-up required.

Losses in the lime-recovery system can be estimated by a technique analogous to that employed for Na. While the sludge analysis does not include a determination of sulfur, the liquid content of the sludge must be essentially white liquor diluted with wash water (the wash water being included in the white-liquor stream). On the assumption that the composition of the total alkali in the sludge is the same as that in the white liquor, losses of S from the lime-recovery system are obtained as follows:

Lb of inerts plus Ca as CaCO_3 in losses	Lb of total alkali (as Na_2SO_4) in losses	Equivalents of total alkali	
67.2	4.3	2	0.55
	48.5	142	4.39
			$\frac{0.55}{4.39} = 0.01 \text{ atom of S}$

By difference, sulfur losses in the burner are

$$1.84 - 0.05 - 0.09 - 0.01 = 1.69 \text{ atoms}$$

In other words, more than 90% of the make-up sulfur added as salt cake and elemental sulfur in the burner feed is lost in the stack gases.

Since the stack gases evidently account for most of the losses of both alkali and sulfur, the next step is to inquire regarding the mechanism by which these losses occur. Some information is provided by the ratio of Na to S in the stack gases. According to the balance above, the atomic ratio of Na to S in these gases is 1.99/1.69, or 1.18. This figure shows that losses cannot be occurring solely in the form of compounds of Na and S, such as Na_2S or Na_2SO_4 , for in that case the ratio would be 2. Apparently a part of the losses must be in another form that is rich in sulfur. The probabilities are that the chief losses from the burner are SO_2 , which is evolved in the earlier stages of concentration and incineration, and Na_2SO_4 fumes, which result from volatilization of Na_2CO_3 and Na_2SO_4 in the later stages, followed by reaction of Na_2CO_3 with SO_2 and

air. If it is assumed that the stack losses are as Na_2SO_4 and SO_2 , then the Na_2SO_4 is $1.99/2$, or 1.00 mol, and the SO_2 is $1.69 - 1.00$, or 0.69 mol. Expressed as a percentage of the sulfur losses in the burner, the estimated amount of sulfur present as Na_2SO_4 fumes in the stack gases is

$$1.00(100)/(1.00 + 0.69) = 59\%$$

The report to the management on the performance of this mill should emphasize that the plant is faced with a serious fume problem, which accounts for a large fraction of the consumption of salt cake. Efforts should be made to change the operation of the burner in such a way as to reduce the formation of fumes within the burner itself. At the same time the installation of improved methods of recovery of fumes from the stack gases should be considered.

With regard to the consumption of sulfur, it should be pointed out that there are considerable losses due to volatilization in the earlier stages of the burning process and these must be due in large measure to the fact that the elemental sulfur in the make-up is volatile at relatively low temperatures. A serious study should be made of various possible methods of adding sulfur to the system, in such a way that the sulfur is introduced in a relatively nonvolatile form.

PROBLEMS

1. A 225-g sample of a certain lime is causticized with 2000 ml of 2.69 *N* soda-ash solution. A 1.25-ml sample is removed from the final solution and titrated with 0.139 *N* HCl. To reach the end point with phenolphthalein 25.66 ml of acid is required, and an additional 1.44 ml to reach the end point with methyl orange. What is the normality of the final solution? What is the per cent conversion of soda ash to caustic?

Ans. 3.01 *N*; 89.4%.

2. A special-purpose caustic soda is being made by causticization of soda ash in a system consisting of a reaction tank, a dissolving tank, a filter, and two thickeners in series. The slurry produced in the reaction tank is pumped continuously to the filter. The caustic liquor obtained as filtrate is sent to evaporators, which produce a mixture of solid NaOH and Na_2CO_3 . The sludge from the filter, which contains approximately 10% of the sodium compounds in the slurry, is fed to the first thickener and from there flows to the second thickener. The sludge leaving the second thickener is substantially free of sodium compounds and carries 1 lb water per pound of dry solids. Fresh water is supplied continuously to the second thickener at the rate of 2.66 lb per pound of fresh Na_2CO_3 fed to the dissolving tank. The overflow from the second thickener is pumped to the first thickener. The wash water overflowing from the first thickener, together with fresh water added directly to the dissolving tank, is used to dissolve the soda ash; and the resulting solution is fed to the reaction vessel. Solid $\text{Ca}(\text{OH})_2$, 10% in excess of that stoichiometrically equivalent to the soda ash, is also fed to the reaction vessel. Past experience indicates that in this particular operation the ratio $(\text{OH}^-)^2/\text{CO}_3^{2-}$ in the liquid phase of the slurry withdrawn from the reaction vessel is approximately 100.

(a) What is the weight per cent Na_2CO_3 in the dry caustic soda?

(b) What is the composition in weight per cent (dry basis) of the sludge discharged from the system?

(c) On the assumption that the caustic liquor obtained from the filter is 3.0 *N* at 20°C, estimate what per cent of the total fresh water supplied to the system is fed to the second thickener.

3. A Vorce cell in good condition and operating smoothly is consuming 1500 amp at 4.34 volts. It is being fed with a solution having a specific gravity of 1.181, containing 24% NaCl and 0.1% HCl, and is producing a lye of 1.142 sp gr, containing 16.32% NaCl, 5.60% NaOH, 0.06% Na₂CO₃, and 0.14% NaClO₃. The composition of the anode gas is 71.95% Cl₂, 5.25% H₂, 1.75% CO₂, 7.20% O₂, and 13.85% N₂. The cathode gas analyzes 80.35% H₂, 5.55% O₂, and 14.10% N₂. The gases are being withdrawn from the cell under a suction of 4 in. of water at a temperature of 42°C, with a partial pressure of water vapor of 2.01 in. Hg. The brine feed is being supplied at the rate of 28.4 liters/hr. The barometer is 752 mm Hg. Compute the following:

(a) Production of Cl₂ gas in pounds per 24-hr day.

(b) Current efficiency of caustic production.

(c) Current efficiency of chlorine production.

(d) Current efficiency of hydrogen production.

4. Data have been reported on the performance of a de Nora mercury amalgam cell, of a type employed in a number of plants in Italy.¹ The unit has two main parts. The first of these is the cell in which brine is electrolyzed between graphite anodes and a mercury cathode to produce chlorine gas and sodium amalgam. The second part is the decomposer, which is a steel tower packed with lumps of graphite. Amalgam flows continuously from the cell to the top of the decomposer, while water is fed continuously to the bottom. Hydrogen gas and a strong caustic solution are withdrawn at the top of the decomposer; at the bottom, regenerated mercury is removed and pumped continuously back to the cell.

Under typical operating conditions the cell is fed with 3 gal/min of brine² containing 310 g/l of NaCl. The depleted brine withdrawn from the cell contains 270 g/l of NaCl. The current is 15,000 amp, the voltage 4.10 to 4.15, the power consumption 3,000 kwhr per short ton of Cl₂, and the temperature of the cell approximately 70°C. The amalgam flowing to the decomposer contains 0.1% Na, and the regenerated mercury only 0.001% Na. The average analysis of the caustic leaving the decomposer is 45% NaOH and 0.95% Na₂CO₃, with a number of minor impurities. Per metric ton of Cl₂ manufactured, 3 kg of graphite are consumed. The air-free Cl₂ gas produced by cells of this type is known to contain approximately 0.5% H₂ and also a small amount of CO₂. Compute the following quantities from the above information:

(a) Production of Cl₂ in metric tons per day.

(b) Current efficiency of chlorine production.

(c) Current efficiency of caustic production.

(d) Current efficiency of hydrogen production.

(e) Rate of circulation of mercury in gallons per minute.

(f) At what point in the system do you think that most of the consumption of graphite is taking place?

5. A Solvay plant with the same flow sheet as that of the plant of Illustration 3 (Fig. 9-3) has the following average operating conditions: The purified brine fed to the brine ammonia scrubber contains 23.1% NaCl. Analysis of the liquid leaving the bottom of the main carbonating tower shows 40 g CO₂, 78.1 g total NH₃, 57.8 g fixed

¹ R. L. Kenyon and P. Gallone, *Ind. Eng. Chem.*, **45**, 1162 (1953).

² *Ibid.*, p. 1171. Calculated from the table on p. 1171 and from the reported concentrations of the feed and the depleted brine.

NH_3 , and 87.9 g NaCl per liter. The wash water leaving the filters contains 0.5% of the solid NaHCO_3 coming from the bottom of the main carbonating towers. The CO_2 content of the dry kiln gas is 44.1%, and of the dry waste gas from the brine ammonia scrubber 2.8%. Loss of NH_3 in the waste gas is negligible. Calculate the following:

(a) The molal ratio of CO_2 to NH_3 in the gases evolved from the ammonia still.

(b) The mols of dry waste gas per 100 lb brine fed to the system.

6. The questions below refer to the Solvay plant of Illustration 3. Neglect the presence of NaCl in the product and of air in the calciner gas.

(a) What is the composition (dry basis) of the CaCl_2 slurry leaving the bottom of the ammonia still?

(b) If the plant undertakes the production of sodium bicarbonate, discontinuing operation of the calciner, how many mols of CaO can be made, over and above the requirements of the process itself, per atom of Cl in the liquid from the main carbonating towers? Grant that the kiln is to be operated to satisfy the CO_2 requirements. As before, 5% excess air will be used; 85% decomposition of the stone will be attained; and the kiln gas will again contain 36.5% CO_2 . The waste gas will contain 6% CO_2 and negligible NH_3 . Washing of the precipitate recovered by filtration will again result in dissolving 1% of the solid NaHCO_3 from the towers.

(c) In order to avoid dilution of the brine with water, the plant dries the gases recovered from the ammonia still before recycling them to the primary ammonia absorber. The dried gases are at 50°C . If cooled, they deposit ammonium carbamate. The sublimation pressure of this material is 171 mm Hg at 34.6°C , 295 mm at 43.2°C , 389 mm at 47.5°C , and 517 mm at 52.2°C . At what pressure in millimeters of mercury must these gases go to the absorber to avoid any possibility of precipitation at 50°C ?

7. In the Solvay plant of Illustration 3 the pressure of the gases entering the bottom of the main carbonating towers is 35 psig, the temperature of these gases is 38°C , and their superficial velocity is 0.132 ft/sec. The specific gravity of the effluent liquid is 1.177, and of the crystal bicarbonate suspended in it 2.20. In order to maintain proper conditions of precipitation to ensure a free-filtering crystal magma, the rate of precipitation of sodium bicarbonate from the liquid in the slurry on the bottom plate of the main carbonating towers must be 18% per hour of the total sodium constituents in the liquid. Of the total sodium bicarbonate produced in the towers 0.5% is precipitated on this plate. On the assumption that the slurry is expanded in volume by the gases rising through it to twice the volume of the slurry itself, calculate the depth, in inches, of liquid on the bottom plate.

8. Experimental measurements of the equilibrium in the Solvay reaction have been reported by Hempel and Tedesco.¹ From a study of the details of the technique that they used in analyzing their solutions, what do you conclude were the constituents that they actually determined?

9. Measurements of the equilibrium in the Solvay reaction have been reported by Neumann and Domke.² From a study of the experimental technique that they employed in analyzing their solutions, what do you conclude were the constituents that they actually determined?

10. Seidell³ gives the following information on aqueous solutions saturated with NaHCO_3 :

¹ *Z. angew. Chem.*, **24**, 2459 (1911).

² *Z. Elektrochem.*, **34**, 136 (1928).

³ A. Seidell. "Solubilities of Inorganic and Metal Organic Compounds," 3d ed., D. Van Nostrand Company, Inc., New York, 1940.

SOLUBILITY OF PURE NaHCO_3 AT 30°C

Dibbits, 1874; Fedotieff, 1904

11.1 g NaHCO_3 /100 g H_2O SOLUTIONS OF NaHCO_3 AND NaCl AT 30°C

Freeth, 1922

g/100 g saturated solution		Solid phase
NaHCO_3	NaCl	
9.9	0.0	NaHCO_3
4.9	8.8	NaHCO_3
1.9	19.5	NaHCO_3
1.2	26.1	$\text{NaHCO}_3 + \text{NaCl}$

Fedotieff

g/1000 g H_2O

NaHCO_3	NaCl
110.2	0.0
72.8	59.9
47.3	121.9
32.0	186.3
22.3	256.0
13.9	358.1

SOLUTIONS OF NaHCO_3 AND NH_4HCO_3

Fedotieff, 1901

Temperature, $^\circ\text{C}$	g/1000 g H_2O	
	NaHCO_3	NH_4HCO_3
15	88.0	0.0
15	80.0	23.0
15	74.6	44.0
15	66.7	85.7
15	59.2	170.6
30	138.6	0.0
30	70.0	230

(a) Employing the data on pure NaHCO_3 and on NaHCO_3 - NaCl solutions, make a plot showing the relation between the grams of H_2O per equivalent of sodium ion and the equivalents of chloride ion per equivalent of sodium ion.

(b) Utilizing the data on NaHCO_3 - NH_4HCO_3 solutions, make a plot showing the relation between the grams of H_2O per equivalent of sodium plus ammonium ions and the equivalents of sodium per equivalent of sodium plus ammonium. On the basis of

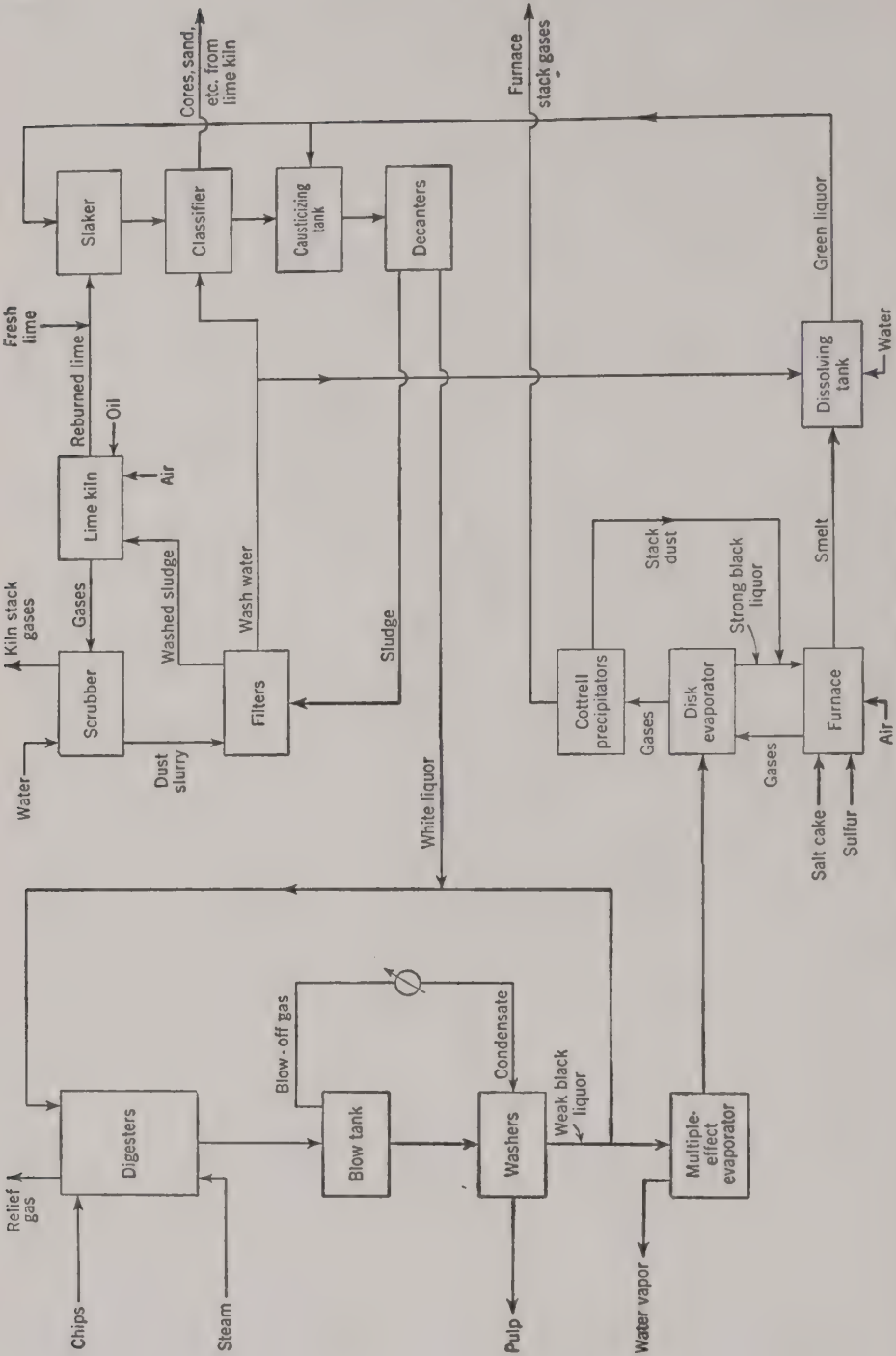


FIG. 9-9. Kraft paper mill of Problem 11.

all the Seidell data on aqueous solutions saturated with NaHCO_3 , what is your estimate of the grams of H_2O per equivalent of sodium plus ammonium ions in a solution of NaHCO_3 and NH_4HCO_3 at 30°C , saturated with NaHCO_3 and containing 0.75 equivalent of sodium per equivalent of sodium plus ammonium?

11. A kraft-paper mill at Port Townsend, Wash., has the flow sheet shown in Fig. 9-9.¹ The mill operates continuously except for the digesters, in which the chips are cooked in a series of batches. During a typical cook a digester is charged with 23.3 tons of chips (12.3 tons on air-dry basis), 760 cu ft of white liquor, and 525 cu ft of weak black liquor, and produces 6.5 tons of pulp. The white liquor contains 12.5% solids and has the following analysis in terms of pounds of equivalent Na_2O per cubic foot: Na_2CO_3 , 1.6; NaOH , 4.1; Na_2S , 1.9; Na_2SO_4 , 0.1; and $\text{Na}_2\text{S}_2\text{O}_3$, 0.05. The weak black liquor contains 15% solids and has a gravity of from 10 to 11°Bé . The net production of weak black liquor (*i.e.*, the liquor leaving the washers less that recycled to the digesters) contains 1800 lb of organic material and 1200 lb of inorganics per ton of pulp manufactured. Each ton of pulp contains an amount of Na_2SO_4 equivalent to 40 lb of Na_2O .

In the evaporation and recovery system the weak black liquor is concentrated to produce strong black liquor, which is mixed with make-up salt cake, make-up sulfur, and stack dust and then charged to the furnace. On a basis of 1 ton of pulp the amounts of salt cake, sulfur, and dust are 100 lb, 15 lb, and 100 lb, respectively. The average analysis of the stack dust is 80% Na_2SO_4 , 15% Na_2CO_3 , 4% Na_2SO_3 , and 1% miscellaneous. The green liquor contains 15% solids and has the following analysis in terms of pounds of equivalent Na_2O per cubic foot: Na_2CO_3 5.2, Na_2S 2.1, NaOH 0.2, Na_2SO_4 0.1, and $\text{Na}_2\text{S}_2\text{O}_3$ 0.05.

In the causticizing system the green liquor from the dissolving tank is divided, approximately half being fed to the slaker and half to the causticizing tank. The slaker is also supplied with 35 lb of fresh lime per ton of pulp and 500 lb of reburnt lime per ton of pulp. The average analysis of the latter is 88% CaO , 8.5% CaCO_3 , 1.5% NaOH , and 2.0% miscellaneous.

Audit the utilization of chemicals in this mill, and submit a brief memo giving your results and conclusions.

¹ F. G. Sawyer, W. F. Holzer, and L. D. McGlothlin, *Ind. Eng. Chem.*, **42**, 756 (1950).

Chapter 10

METALLURGY

The roasting of sulfide ores is typical of the metallurgical operations where problems concerned with quantities of air, products, and the like may be solved by stoichiometric methods. The roasting of FeS_2 has already been treated in Chap. 6, and the roasting of sulfides of other metals may be treated by similar techniques. It seems unnecessary, therefore, to discuss the minor stoichiometric differences that exist among the various sulfides. This chapter is concerned primarily with another important problem, namely, the reduction and refining operations in the metallurgy of iron. The methods of computation are applicable to similar reactions in the treatment of other metals as well as to the more general problem of gas-solid reactions.

Illustration 1. The following figures are abstracted from the data sheet of a test on a blast furnace using hematite ore:

DATA	
Reduced to 24-hr basis	
Burden:	
Ore.....	2,150,000 lb
Coke.....	1,048,500 lb
Scale.....	151,800 lb
Stone.....	414,000 lb
Flue dust (dry basis).....	120,000 lb
Pig.....	1,203,600 lb
Barometer.....	29.84 in.
Air temperature.....	72°F
Relative humidity.....	82%
Average blast pressure.....	14.1 psig
Average blast temperature.....	960°F
Average top-gas temperature.....	330°F

ANALYSES			
	<i>Per cent</i>		<i>Per cent</i>
Ore:		Scale:	
Fe.....	51.6	Fe.....	72.68
Mn.....	0.83	Mn.....	0.57
S.....	0.032	Pig:	
H ₂ O.....	10.6	Fe.....	92.12
SiO ₂	8.78	Si.....	1.36
Coke:		Mn.....	1.49
Fixed carbon.....	80.7	S.....	0.027
Vol. comb. matter.....	2.2	C.....	4.65
Moisture.....	4.4	Flue dust:	
Ash.....	12.7	Fe.....	41.4
Total C (combined).....	82.14	C.....	7.9
Total H (combined).....	0.83	Gas:	
Btu/lb, 12,130		CO ₂	14.1
Limestone:		CO.....	24.6
CaO.....	54.55	O ₂	0.1
SiO ₂	0.80	H ₂	2.2
Moisture.....	0.70	N ₂	59.0
Ignition loss.....	43.30		

Discussion. From the data as presented, it is immediately possible to set up an iron balance, which will give a check on the accuracy of the data:

IRON BALANCE		<i>Pounds</i>
Input:		
Ore, 2,150,000(0.516).....		1,109,400
Scale, 151,800(0.7268).....		110,000
Total.....		1,219,400
Output:		
Pig, 1,203,600(0.9212).....		1,108,800
Dust, 120,000(0.414).....		49,600
Deficiency.....		61,000
Total.....		1,219,400

The calculation shows that the output of iron is about 5% less than the input. This may be due partly to iron in the slag, largely as emulsified nodules of pig. There is also the likelihood that the pig withdrawn from the furnace did not quantitatively correspond to the charge fed at the top. On a blast furnace it is necessary to have a long test period in order to make this error negligible.

It is also possible to set up a carbon balance that will give the carbon in the gas by difference.

CARBON BALANCE

	Pounds
Input:	
Coke, 1,048,500(0.8214).....	861,200
Stone, 414,000(0.4330)(12/44).....	48,900
Total.....	910,100
Output:	
Pig, 1,203,600(0.0465).....	56,000
Dust, 120,000(0.079).....	9,500
Gas, by difference.....	844,600
Total.....	910,100
$(844,600/12)(100/38.7) = 181,900$ mols dry top gas	

Since the iron balance is out by 5%, the carbon balance may include a similar discrepancy. Therefore, it is advisable to compute the quantity of top gas by an oxygen balance to see if a check can be obtained on the above result. The oxygen content of the gas depends not only on reactions of air oxygen with carbon and hydrogen but also on reactions of these elements with oxygen in the charge. The first step, then, is to recompute the analyses of the various materials to show the oxygen content, or the oxygen equivalent to the elements that enter into reaction with it.

Basis: 100 lb coke.

Atoms C, 82.14/12.....	6.85
Mols total H ₂ , 0.83/2.016.....	0.411
Mols H ₂ O, 4.4/18.....	0.244
Mols net H ₂ , 0.411 - 0.244.....	0.167
Ratio, (net H ₂)/C, 0.167/6.85.....	0.0244

Basis: 100 lb ore.

The ratio of O/Fe in pure hematite is 3:2. Assuming Mn in the ore as MnO₂ and neglecting sulfur, the oxygen removed in reducing the ore is:

	Atoms	Factor	Atoms O
Fe: 51.6/55.84.....	0.925	$\times \frac{3}{2}$	1.387
Mn: 0.83/54.93.....	0.015	$\times 2$	0.030
Total.....	1.417
Ratio, O/Fe, 1.417/0.925.....			1.532

Basis: 100 lb scale.

The scale contains 72.68% Fe and 0.57% Mn. No serious error will be made if the remainder, 26.75%, is considered to be all oxygen. The composition of 100 lb of scale is, therefore, as follows:

	<i>Atoms</i>
Fe: 72.68/55.84.....	1.302
Mn: 0.57/54.93.....	0.010
O: 26.75/16.00.....	1.672
Ratio, O/Fe, 1.672/1.302.....	1.285

Basis: 100 lb pig. Oxygen removed by reduction.

Since the iron comes from two sources, ore and scale, it will be assumed that the quantities coming from each are in the same ratio as the iron contents of the measured quantities of the charge.

<i>O removed from</i>	<i>Atoms</i>
Ore, (92.12/55.84)(1,109,400/1,219,400)1.532*.....	2.299
Scale, (92.12/55.84)(110,000/1,219,400)1.285*.....	0.191
Si, (1.36/28.1)2.....	0.097
Total O removed by reduction.....	2.587
Total per 24 hr, 1,203,600(0.02587).....	31,200 atoms

The oxygen from the air and charge and the elements that react with it, such as carbon and hydrogen, are tied together in the gas from the furnace. At this point one may turn to the gas and use it as the basis for continuing the calculations.

* Note that this oxygen includes that from reduction of manganese oxides. The oxygen equivalent to the Mn in the pig can, of course, be computed separately from that equivalent to the iron, but this requires making an assumption regarding the state of oxidation of the Mn. This has already been allowed for when the analyses of the ore and scale were recomputed to an atomic basis. To show that the method of computation is substantially in accord with other data, the manganese can be checked by an independent balance as follows:

Basis: 24 hr.

	<i>Pounds</i>
Mn from ore, 2,150,000(0.0083).....	17,850
Mn from scale, 151,800(0.0057).....	870
Total input.....	18,720
Mn in pig, 1,203,600(0.0149).....	17,920
Deficiency.....	800
Total.....	18,720

This balance shows about the same discrepancy between input and output as does the iron balance.

Basis: 100 mols dry gas.

Gas	Mols	Atoms C	Atoms O	Mols N ₂
CO ₂	14.1	14.1	28.2	
CO.....	24.6	24.6	24.6	
O ₂	0.1	0.2	
H ₂	2.2	2.2
N ₂	59.0			
Total.....	100.0	38.7	53.0	2.2
C from stone, 38.7(49,000/844,500)*.....		2.25		
C from fuel, by difference.....		36.45		
O from stone, 2(2.25).....			4.50	
O \approx N ₂ , 59.0(42/79).....			31.35	
Net H ₂ from coke, 36.45(0.0244).....			0.89
H ₂ from decomposition of H ₂ O, by difference.....			1.31
O from decomposition of H ₂ O.....			1.31	
Total O accounted for.....			37.16	
O from reduction of ore and scale, by difference.....			15.84	
			53.0	

* Figures obtained from the carbon balance. With this exception, the computation of O from reduction of ore and scale is an independent calculation.

Top gas is computed from the oxygen balance as follows:

Basis: 24 hr.

$$\frac{\text{Atoms O}}{31,200} \bigg| \frac{100}{15.84} = 197,000 \text{ mols dry top gas}$$

While the carbon and oxygen balances are based on analyses of the same materials, they are none the less independent except for the fact that in the oxygen balance the oxygen from the stone had to be computed from carbon data. The difference between the two values for the top gas, 181,900 mols and 197,000 mols, about 8%, is a reasonable measure of the dependability of the data. The carbon balance, however, ought to be given more weight than the other, because on the gas basis oxygen from the ore represents a difference between relatively large quantities. Unless expensive equipment is available to measure the huge volume of gas leaving the furnace, balances of this sort represent by far the easiest and most accurate method of determining its amount. See Fig. 10-1 for a diagrammatic representation of this problem.

It is instructive to compute the following quantities:

1. Volume of top gas leaving the furnace per minute
2. Volume of free air per minute at the blower intake, neglecting any possible leakage between the blower and the furnace
3. Btu as potential heat of combustion in the furnace gas, expressed as per cent of the heat of combustion of the fuel
4. Percentage of the carbon in the coke charged that is burnt at the tuyeres

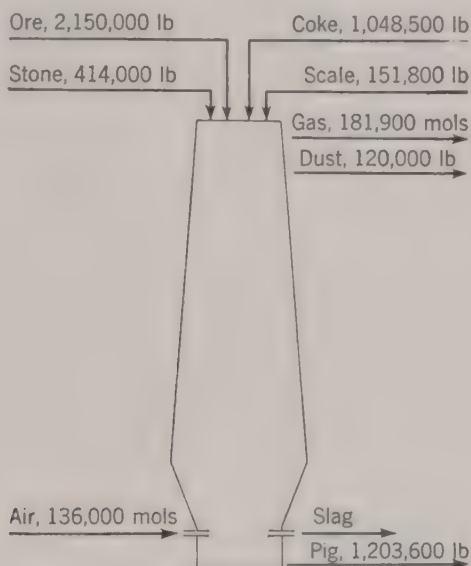


FIG. 10-1. Blast-furnace problem. Basis: 24 hr.

1. *Volume of top gas.* First compute the amount of water vapor in the air, that from the charge, and that formed on combustion of the coke, and then deduct from the sum of these three the equivalent of the H_2 in the gas.

Basis: 24 hr.

Mols of water vapor.

a. From air: $72^\circ F$, 82% relative humidity;

$$\text{Partial pressure of } H_2O \text{ vapor} = 0.82(0.79) = 0.65 \text{ in. Hg}$$

$$\text{Partial pressure of dry air} = 29.84 - 0.65 = 29.19 \text{ in. Hg}$$

Mols dry gas	Mols N_2	Mols dry air	
181,700	59.0	100	$\frac{0.65}{29.19} = 3,020 \text{ mols } H_2O$
	100.0	79	

b. From ore:

$$2,150,000(0.106)/18 \dots\dots\dots 12,650 \text{ mols H}_2\text{O}$$

c. From coke:

$$\begin{array}{r} 1,048,500 (0.411/100) \dots\dots\dots 4,310 \text{ mols H}_2\text{O} \\ \hline 19,980 \text{ mols H}_2\text{O } (a + b + c) \\ \text{Leaving as H}_2, 181,700(0.022) \dots\dots\dots 4,000 \text{ mols} \\ \hline \text{Left as H}_2\text{O} \dots\dots\dots 15,980 \text{ mols H}_2\text{O} \\ \text{Dry gas} \dots\dots\dots 181,900 \text{ mols} \\ \hline \text{Total gas} \dots\dots\dots 197,880 \text{ mols} \end{array}$$

Basis: 1 min.

Mols gas per min	Cu ft s.c.	At 330°F	
197,880	359	790	29.92
(24)(60)		492	29.84

$$= 79,400 \text{ cu ft/min}$$

2. Volume of free air per minute at the blower intake.

Mols dry gas	Mols N ₂	Mols air	Cu ft d.s.c.	Dry at 72°F, 1 atm	
181,900	59.0	100	359	532	29.92
(24)(60)	100.0	79		492	29.19

$$= 37,600 \text{ cu ft/min}$$

3. Btu as potential heat of combustion in the furnace gas.

Basis: 1 mol dry top gas.

Gas	Mols	Molal heat of combustion, Chu	Product
CO.....	0.246	67,600	16,600
H ₂	0.022	68,300	1,500
Total.....	18,100

$$(181,900)(18,100)(1.8) = 5,920,000,000 \text{ Btu potential heat.}$$

$$\text{Heat input, } (1,048,500)(12,130) \doteq 12,720,000,000 \text{ Btu}$$

Potential heat of combustion as per cent of the heat input:

$$(5,920,000,000/12,720,000,000)100 = 46.5\%$$

Of every 100 heat units charged to the furnace as heat of combustion of the coke, 46.5 units leave the furnace as potential heat of combustion in the gas. It must, however, be remembered that heat also enters the furnace as sensible heat in the blast, and this fact must be taken into account when getting the complete picture of heat distribution.

4. *Percentage of the carbon in the coke charged that is burnt at the tuyeres.* At the very high temperature of the bottom of the blast furnace, CO_2 , which is formed in the immediate vicinity of the tuyeres, is reduced with extreme rapidity by contact with more carbon, substantially completely to CO . This must be the condition in the bottom of the furnace, since CO_2 , if present in quantity, would reoxidize the iron to the oxide. It therefore follows that in the tuyere zone there must be consumed an amount of carbon substantially equivalent to quantitative conversion of the oxygen in air to CO . There is actually consumed an additional amount corresponding to the conversion of some of the nitrogen to cyanogen, but this will be neglected. (These reactions are further discussed in Illustrations 2 and 3.)

Mols dry gas	Mols N_2	Atoms O = atoms C	Lb coke	
181,900	59.0	42.0	100	100
	100.0	79.0	6.85	1,048,500 = 79.6%

Blast-furnace shaft-gas analyses. By the use of suitable techniques, it is possible to withdraw gas samples from various locations within the shaft of a blast furnace. The analyses of these gas samples can be used to throw considerable light on the nature of physical and chemical processes occurring in the shaft, as will be shown in the following examples. In addition to their significance for metallurgical operations, the general methods of attack employed in these examples are useful in a wide variety of situations involving countercurrent contact of solid and gaseous streams.

Illustration 2. A number of years ago the Bureau of Mines¹ conducted a series of tests on 13 blast furnaces, differing considerably in construction and operation, in which they collected in each furnace a series of gas samples all taken at the level of the tuyeres but at different distances from the nose of the tuyeres radially inward toward the center of the furnace. The data, even on analyses of gas samples taken at different times at a given point in a given furnace, scattered widely. However, when the individual analyses are plotted against the distance radially inward from the nose of the tuyere, even with the data for all the furnaces on a single plot, the general trend cannot be mistaken despite the scattering of the points.² The Bureau averaged all the

¹ G. St. J. Perrott and S. P. Kinney, *Trans. Am. Inst. Mining Met. Eng.*, **69**, 543 (1923).

² The scatter of the experimental results is to be expected considering the operating conditions existing at the tuyere level of the furnaces. The furnace at this point is filled with lumps of coke, which are being consumed, allowing the charge to settle so that the lumps are continually being replaced by fresh ones sliding down from above. This means that the gas-flow pattern through this part of the furnace is highly irregu-

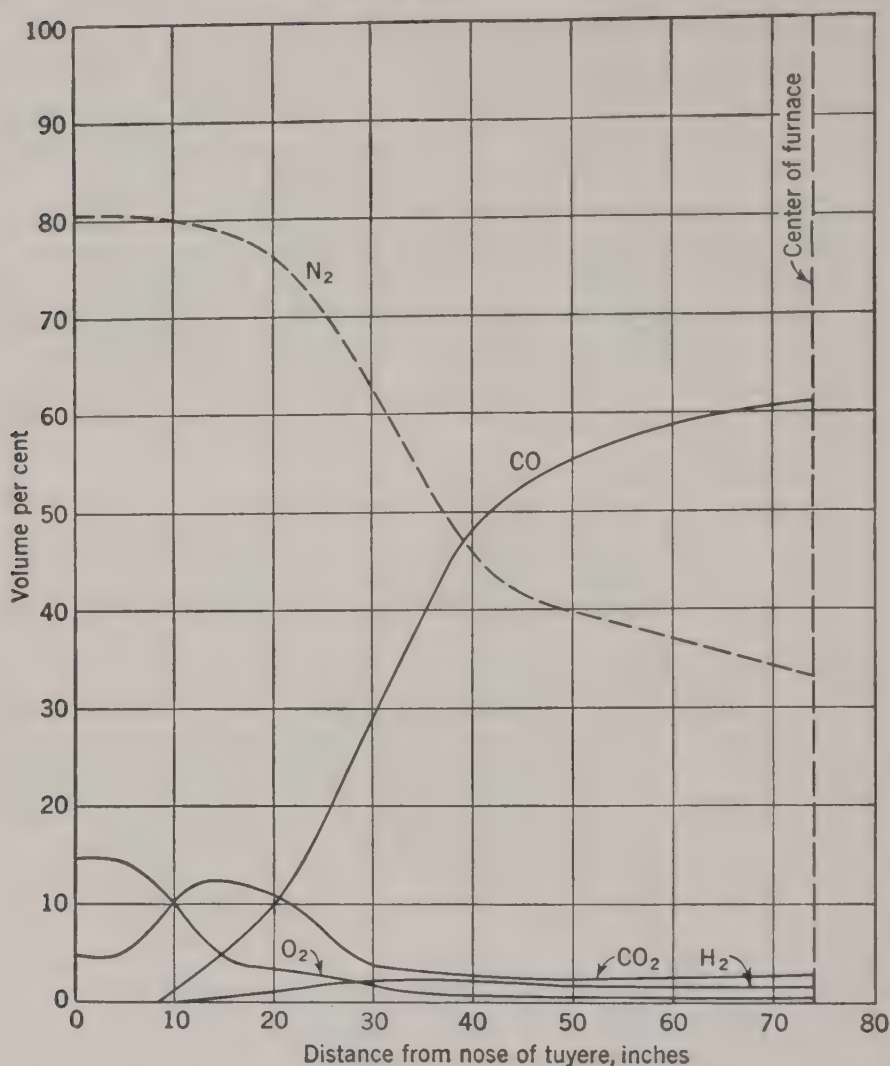


FIG. 10-2. Horizontal survey of blast-furnace gases at the tuyere level.

numerous analyses taken at each individual point in each furnace, plotted these averages against the radial distances, and for each furnace drew smooth curves among the points. Again, these curves all have common trends and shapes.

Figure 10-2 reproduces the smooth curves of the Bureau for Alabama and continually changing. This is probably particularly true of the horizontal component of velocity. This change in flow pattern is sure to have a profound effect on gas composition at a given point as time goes on, although in the long run the average composition will settle down to a quite definite value. Moreover, the problem of collecting a representative sample is very real. For example, at the high temperature levels in the furnace, the authors report frequent burning out and fusion of the water-cooled gas sample tubes. In consequence of all this, the significance of a single analysis is almost negligible, but statistical averages can be relevant and important.

Furnace No. 2 for O_2 , CO_2 , and CO . The Bureau did not plot the data that they reported for hydrogen or nitrogen. The hydrogen curve shown on Fig. 10-2 has been obtained by the method that they used for the curves that they did show. The nitrogen curve on this figure is obtained by difference from the sum of their average curves and 100, rather than being independently drawn by eye through the averages of the nitrogen points. These curves, then, are representative of the Bureau of Mines data, except that the values for CO_2 shown in this figure are definitely higher toward the middle of the furnace than is characteristic of their data as a whole. The general trend of their data on samples taken more than halfway in toward the center of the furnace was toward negligible levels of CO_2 .

What conclusions can one draw from the curves of Fig. 10-2?

Discussion. In interpreting these data one must keep in mind that the nitrogen in the samples came from the air blown into the tuyeres. The nitrogen is unaffected by the reactions occurring in the furnace (except for the formation of a small amount of cyanogen). Consequently, in view of the fact that gases once mixed do not segregate spontaneously, it is legitimate to use a nitrogen base for the correlation and interpretation of the analyses. The data have been recalculated and tabulated below.

Basis: 100 mols N_2 .

	Radial distance from tuyeres, in.								
	0	10	20	30	40	50	60	70	74 (centerline)
CO_2	6.2	12.5	14.5	6.5	5.4	5.0	6.0	8.0	9.0
CO	0	1.2	13.0	46.0	105	138	160	180	185
O_2	18.0	12.5	4.2	3.1	1.0	1.0	0.5	0.5	0.5
H_2	0	0	1.3	2.4	4.4	4.0	3.0	4.0	4.5

In the immediate neighborhood of the tuyeres, from 0 to 10 in. in, it is evident from the disappearance of O_2 and appearance of CO_2 that the major process occurring there is combustion of coke by air, according to the over-all reaction $C + O_2 = CO_2$. From 20 to 40 in. in, reaction of O_2 is practically completed. Meanwhile the CO_2 is depleted as CO is formed by the over-all reaction $CO_2 + C = 2CO$. In the remainder of the distance to the center, the only significant reaction is an increase in the amount of CO in the gas. Since there is no possible source of CO in the gas itself in this region, the CO must be evolved from the solid phase. Thus, there are three rather definite zones, the first being a region in which the predominant reaction is combustion of coke to form CO_2 , the second characterized by reduction of CO_2 to CO by coke, and

the third a region in which CO is evolved from the solid phase in the furnace.

If the above conclusions as to what goes on at the tuyere level of the furnace are correct, it should be possible to check the data to see if they satisfy the stoichiometric relationships implied by the postulated reactions. For example, if the only reaction occurring between the tuyeres and 10 in. in is $C + O_2 = CO_2$, then the appearance of CO_2 should equal quantitatively the disappearance of O_2 . Furthermore, the sum of the free O_2 and CO_2 should equal the O_2 originally present with the N_2 in the entering air. In the second zone, where the reaction $C + O_2 = CO_2$ is completed and CO_2 is reduced by carbon to CO, the sum of the O_2 present as free O_2 , CO, and CO_2 should still remain equal to the O_2 originally present in the entering air.

For purposes of making a quantitative check on the reactions it is convenient to calculate ΣO , the sum of the atoms of oxygen present in whatever form, at each sampling point in the furnace. At the same time, it is informative to list ΣC . Thus, at zero distance from the tuyeres, ΣO , on a basis of 100 mols of N_2 , is $2(6.2 + 18.0) = 48.4$, while $\Sigma C = 6.2$. In the entering air, $\Sigma O = 100(2)(21/79) = 53.2$. The results of the calculations for the various sampling points are summarized below.

Basis: 100 mols N_2 .

	Air	Radial distance from tuyeres, in.								
		0	10	20	30	40	50	60	70	74
ΣO	53.2	48.4	51.2	50.4	65.2	117.8	150	173	197	204
ΣC	0	6.2	13.7	27.5	52.5	110.4	143	166	188	194
ΣH_2	0	0	0	1.3	2.4	4.4	4.0	3	4	4.5

Inspection of the figures in the line for ΣO reveals that the total oxygen in the gas, far from remaining constant, as required by the reactions $C + O_2 = CO_2$ and $CO_2 + C = 2CO$, decreases appreciably in the zone near the tuyeres and then increases markedly as the gas flows in to the center of the shaft. Clearly, chemical reactions other than the two reactions already mentioned must be taking place. In the first zone the reaction must be of such a character as to result in a net transfer of oxygen from the gas to the solid phase, while in the second and third zones the reaction must be one that causes a net transfer of oxygen from the solid phase to the gas phase.

The figures in the line for ΣC likewise indicate that the gas analyses are not quantitatively consistent with the hypothesis that the reactions

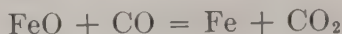
at the tuyere level are $C + O_2 = CO_2$, followed by $CO_2 + C = 2CO$. If these were the only reactions occurring, the maximum amount of carbon that could possibly be gasified would be the number of atoms equivalent to the oxygen in the entering air, *i.e.*, 53.2 atoms of carbon per 100 mols of N_2 . It is evident that the carbon actually gasified is considerably in excess of this figure. Therefore, the reactions occurring in the shaft must account not only for the observed variations in ΣO but also for the gasification of carbon by means other than oxidation by O_2 or by reaction with CO_2 .

The decrease in the total oxygen of the gas in the zone near the tuyeres can be explained on only one basis: oxygen must be consumed by the solid phase, by some substance whose oxidation product is a solid and not a gas. At this point in the furnace, the only substance that can do this is metallic iron, and the reaction must be $2Fe + O_2 = 2FeO$. Evidently, this reaction must be extraordinarily rapid initially, because at zero distance from the tuyeres the oxygen content of the gas is already below that of air. In all probability the samples reported at zero distance were taken at a point that was slightly in from the nose of the tuyeres, because of the difficulty of placing the sampling tube exactly at the nose.

In like manner the increase in total oxygen content of the gas as it moves in toward the center of the shaft can be explained only on the basis that oxygen is evolved from the solid phase by some reaction. So far as the stoichiometry of the situation is concerned, the increases in oxygen and carbon contents of the gas, resulting from the appearance of large amounts of CO in the third zone of the shaft, might be explained by evolution of CO_2 from limestone, followed by rapid reduction of the CO_2 by coke. However, this explanation can be ruled out because the decomposition temperature of $CaCO_3$ is considerably below the temperature at the level of the tuyeres, and it is well established that the limestone is thoroughly decomposed at higher levels in the shaft, above the tuyeres. The only other possible source of oxygen from the solid phase is from reduction of an iron oxide. At the same time, it is known that the lowest oxide of iron, FeO , is reducible by CO at temperatures somewhat lower than those at the tuyeres, and that, in fact, by the time the charge has worked its way down to the tuyeres, the iron oxides have all been reduced to metal. Hence, the iron oxide that is being reduced in the second and third zones must come from some source other than the charge descending from above. In view of the fact that iron oxide is being formed in the neighborhood of the tuyeres, where the concentration of O_2 is high, it seems reasonable to infer that the oxide thus formed near the tuyeres is the source of the oxide undergoing reduction in the center of the shaft. Now, what is the reaction for this iron oxide reduction?

Since it is obvious from the first table that there is no net production of

CO₂ in the center of the shaft and the net product of the reduction reaction is CO, the reaction must be either $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$, or



and if the latter it must be immediately followed by the reaction



Inasmuch as the analyses in the second zone indicate that the reduction of CO₂ by C proceeds at a relatively slow rate at the tuyere-level temperature even when there is a significant concentration of CO₂, it appears that the reduction of FeO in the third zone, and probably also in the second zone as well, is being carried out by reaction with solid carbon.

While the above interpretation accounts qualitatively for the decrease in ΣO near the tuyeres, followed by an increase as the gas passes in toward the center of the shaft, it does not explain the facts that ΣO in the center of the furnace exceeds the oxygen contained in the entering air and that ΣC exceeds the amount equivalent to the oxygen in the air. In this connection the point to remember is that the choice of 100 mols of N₂ as a basis does not imply that the nitrogen in the gas reaching the center of the shaft at the tuyere level is the same in amount as the nitrogen in the air supply to the tuyeres. One can picture the entering air as consisting of a number of elements or "slugs." As the air passes in toward the center of the shaft it has a vertical component of velocity, with the result that elements of the gas are progressively lost in the upward direction and relatively few of the slugs that enter at the tuyeres ever reach the central part of the shaft, at the plane of the tuyeres. However, in each slug that actually does get to the center, the mols of N₂ are substantially the same in number as those contained in that particular slug when it was in the entering air. Hence, the use of a basis of 100 mols of N₂ is legitimate for the purpose of obtaining information on the history of a typical element of gas moving horizontally inward at the level of the tuyeres, but there is no reason to expect that the total number of mols of N₂ reaching the center is equal to that entering the tuyeres. Instead, the number of mols of N₂ reaching the center is much less. Therefore, while the actual number of atoms of oxygen added to the gas phase in the center cannot be greater than the atoms abstracted from the gas phase near the tuyeres, the effect on the gas analysis is magnified by the fact that the oxygen is added to a relatively small amount of gas.

In view of the fact that the distance from the rim to the axis of the shaft may be as much as 6 ft or more, the question may be asked as to the mechanism by which FeO formed in the former region is transferred to the latter. One possibility is mechanical entrainment of FeO in the

blast of air injected into the furnace at high velocity. However, this explanation seems unlikely, because of the obstructed and tortuous path the gas must follow through the lumps of coke, which fill the shaft at the tuyere level. The more probable explanation is the existence of a thermosiphon circulation in the pool of liquid slag and metal contained in the hearth of the furnace, below the tuyeres. It seems most reasonable to suppose that FeO formed near the tuyeres dissolves in the liquid slag descending the shaft and is carried down to the hearth in the stream of liquid metal and slag. Through observation windows at the tuyere level, molten material can be seen trickling down over lumps of coke. In the region of the hearth underneath the tuyeres, the liquid bath is relatively cool, because of heat losses through the walls of the furnace, whereas the center of the bath is relatively hot. As a result of the difference in temperature, there is also a difference in density, which tends to cause the hot, less dense liquid in the center to rise to the surface of the bath and spread out toward the walls, while the colder, denser liquid near the walls tends to sink to the bottom and flow in toward the center. Carried from the walls to the center of the shaft by this mechanism, the FeO can then be reduced through contact of the slag with the lumps of coke, which fill the hearth and support the weight of the descending column of charge in the shaft. CO evolved in the hearth must of necessity pass up the shaft and appear in the gas sampled at the level of the tuyeres.

The conclusions that have been drawn from the above analysis of the data have an extremely practical bearing, when it comes to judging the worth of various proposals that have been made for modifying the construction of a blast furnace. Clearly, modifications must be of such a nature that they do not interfere with the present mechanism for reducing FeO formed near the tuyeres, or else they must provide some equally effective means for achieving the same results.

The appearance of H_2 in the gas analyses remains to be explained. Since any free water in the ore, stone, and coke is distilled at relatively low temperatures, considerably above the tuyeres, the only remaining possible sources are chemically combined H_2 in the coke and decomposition of H_2O vapor in the air. There is some evidence that suggests that most of the H_2 in coke is evolved before the coke reaches the tuyere level (see page 344). Furthermore, the magnitude of the H_2 formed corresponds approximately to what could be obtained from decomposition of air of typical humidity. On the assumption that the highest value of H_2 reported, 4.5 mols per 100 mols of N_2 , corresponds to complete decomposition of H_2O vapor in the entering air, the calculated humidity in pounds of water per pound of dry air is $4.5(18)(0.79/100)(29) = 0.019$. This is a typical value for the humidity of air in many steel-manufacturing regions of the United States.

Illustration 3. The following data have been reported on the performance of a Silesian blast furnace, operating on a mixed charge of various iron ores and slags.¹ The coke contained 75% carbon and the pig 91% iron.

Analyze and interpret these data.

Height above tuyeres, m	Pressure, atm gauge	$t, ^\circ\text{C}$	Per cent CO_2	Per cent CO	Per cent H_2	Per cent CH_4	Per cent N_2
1.0	0.250	1715	0.25	34.0	0.85	0.20	64.70
2.5	0.225	1010	0.35	35.6	0.95	0.25	62.85
4.7	0.150	860	1.05	34.9	0.95	0.40	62.70
10.0	0.082	738	2.00	34.6	1.00	0.45	61.95
13.9	0.038	660	3.00	34.0	1.15	0.40	61.45
18.5 (top)	0.0076	160	7.4	30.3	2.6	0.40	59.3

Discussion. It is evident that the gases rising through the shaft of a blast furnace undergo progressive changes both in composition and amount and that, therefore, the analyses are not reported upon a comparable basis. The first step in an evaluation of the data is to convert the figures to a basis that can be presumed to be constant. Carbon, oxygen, and hydrogen are all involved in reactions between the gas and solid streams. However, all the nitrogen in the gas at any stage comes from the air and flows upward through the shaft in a single stream. Hence, as in the preceding illustration, nitrogen offers a logical basis for computation. A tabulation of the analyses is given below.

Basis: 100 mols N_2 .

Height above tuyeres, m	$t, ^\circ\text{C}$	$\frac{100 \text{ CO}_2}{\text{N}_2}$	$\frac{100 \text{ CO}}{\text{N}_2}$	$\frac{100 \text{ H}_2}{\text{N}_2}$	$\frac{100 \text{ CH}_4}{\text{N}_2}$
1.0	1715	0.4	52.5	1.3	0.3
2.5	1010	0.6	56.6	1.5	0.4
4.7	860	1.7	55.6	1.5	0.6
10.0	738	3.2	55.9	1.6	0.7
13.9	660	4.9	55.4	1.9	0.7
18.5 (top)	160	12.5	51.1	4.4	0.7

Between the 1.0- and 2.5-m levels, the table shows that the principal change consists of an increase in the CO content of the gas stream. As far as the stoichiometry of the situation is concerned, appearance of CO

¹ F. Ullmann, *Enzyklopädie der technischen Chemie*, Vol. 4, p. 376, Urban and Schwarzenberg, Berlin, 1916. The N_2 values have been adjusted slightly to make the total of the various constituents add up to 100.

might be due to the decomposition of limestone followed by reduction of the evolved CO_2 by carbon, or it might indicate that difficultly reducible solid oxides are being reduced by carbon. However, it is known from the decomposition pressure of CaCO_3 and experience with lime kilns that limestone decomposes at temperatures lower than those existing between the 1.0- and 2.5-m levels. It may be concluded that in this region of the shaft reduction of difficultly reducible solid oxides by carbon is occurring.

In the region between 2.5 and 13.9 m, the chief phenomenon is seen to be an increase in the CO_2 content of the gas stream, while at the same time there is little change in the amount of CO. An increase in CO_2 without a corresponding change in CO can occur through decomposition of limestone, or through reduction of solid oxides by CO, followed by reduction of half the CO_2 by carbon to replace the CO reacting with the solid oxides. Considering temperatures, it is probable that decomposition of CaCO_3 cannot be appreciable above the 10.0-m level but may be appreciable just below it, while reduction of easily reducible oxides in the ore is probably not taking place below the 10.0-m level. It will be noted that this statement implies the occurrence of appreciable decomposition of stone at temperature levels in the furnace that are considerably lower than those required for decomposition of limestone in a lime kiln. For example, a certain amount of decomposition of CaCO_3 appears to be taking place in the 4.7- to 10.0-m section at temperatures of 738 to 860°C, whereas in lime-kiln operation it is found that the stone is not decomposed until heated to temperatures in excess of 900°C. The explanation for this difference lies in the fact that when limestone is at temperatures such that the equilibrium partial pressure of CO_2 is less than atmospheric, the rate at which CO_2 is evolved is controlled by the rate at which it can diffuse through the porous CaO formed on the surface of the lumps from the undecomposed CaCO_3 in the interior. Since the gas contained in the pores of the CaO phase is stagnant, diffusion of CO_2 through it, under the influence of the difference in partial pressure of CO_2 between the CaCO_3 surface and the gas at the outside surface of the lump, is slow. In a lime kiln, the only way to obtain a reasonable rate of decomposition and satisfactory capacity is to heat the charge to a temperature in the neighborhood of 900°C, where the decomposition pressure becomes equal to 760 mm and the material "boils." In a blast furnace, on the other hand, the rate of throughput is limited by other factors and is very low compared to that in a lime kiln. The stone is in the furnace for a much longer time so that it is possible for it to decompose by the diffusion mechanism, as long as the temperature is high enough to give a significant difference between the partial pressure of CO_2 at the CaCO_3 surface and the partial pressure of CO_2 in the shaft gases. Above the

10.0-m level, the partial pressure of CO_2 over CaCO_3 and CaO is so low that decomposition must be negligible.

The foregoing points are brought out clearly by reference to Fig. 10-3. The equilibrium line in this figure is based on data from International

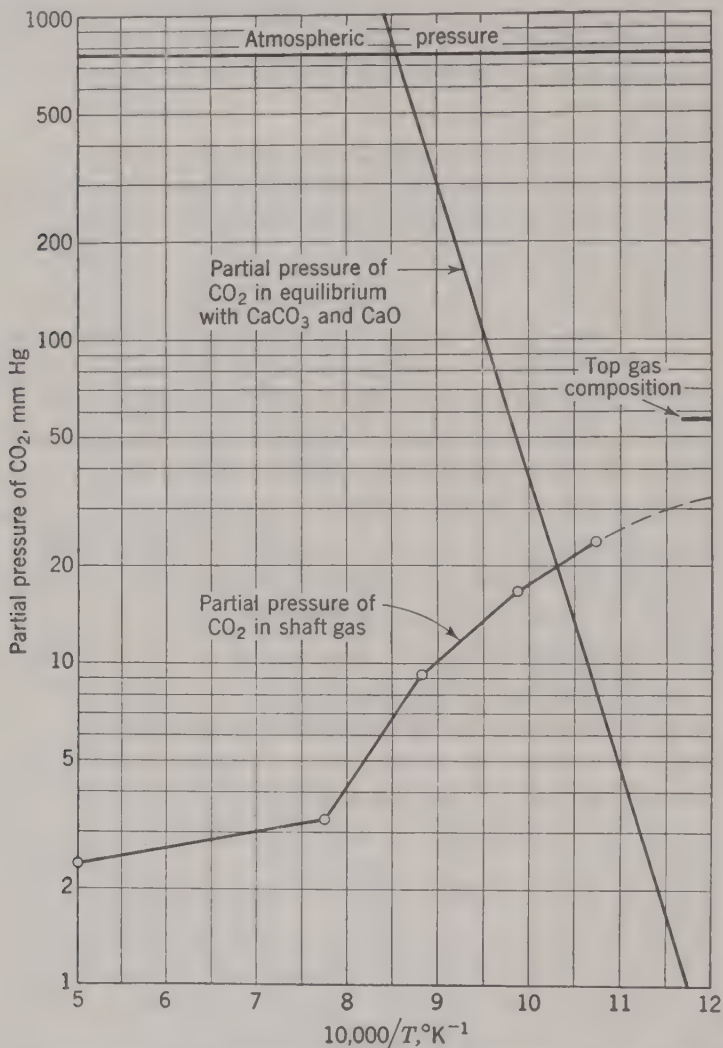


FIG. 10-3. Comparison of blast-furnace shaft-gas analyses with equilibrium of the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$.

Critical Tables.¹ As shown by the plot, the partial pressure of CO_2 over CaCO_3 is less than the partial pressure of CO_2 in the shaft gases at all temperatures in the shaft up to 700°C . Therefore, there can be no decomposition below this temperature level. Actually, the steep portion of the lower curve is located at temperatures just above the point

¹ International Critical Tables, Vol. VII, p. 297, McGraw-Hill Book Company, Inc., New York, 1930.

where the decomposition pressure of CaCO_3 equals 1 atm, indicating that the major part of the decomposition occurs by the "boiling" mechanism.

From the 13.9-m level to the top of the shaft, there is not only a marked increase in the CO_2 content of the gas, but also a considerable decrease in the amount of CO. The CO must be used up in reducing easily reducible oxides in the charge, but if this were the only reaction occurring, the CO_2 formed should equal the CO consumed. Actually, the table on page 340 shows an increase in mols of CO_2 greater than the loss in mols of CO. Therefore, reduction of iron oxides with CO cannot be the only reaction occurring in this section. As explained above, it is impossible for any appreciable evolution of CO_2 from limestone to take place above the 10.0-m level, and hence one must look elsewhere to explain the lack of equivalence between CO loss and CO_2 gain. The simplest explanation is that as the partial pressure of CO_2 builds up in the ascending gases, as a result of evolution of CO_2 from the stone and from reduction of ore by CO, the producer gas reaction, $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$, begins to take place to a significant extent. This reaction manufactures 2 mols of CO for every mol of CO_2 consumed, and tends to replace CO consumed by ore reduction. The net result of the balance between the two types of reaction is a build-up of CO_2 .

If in addition to noting changes in the amount of major constituents as the gas moves up the shaft, one also considers variations in the total amount of each element, it is possible to extract further information from the data. The following table is derived from the gas analyses. The first horizontal line in the table is calculated from the known composition of air.

Basis: 100 mols of N_2 .

Height above tuyeres, m	$t, ^\circ\text{C}$	$\frac{100\Sigma\text{C}}{\text{N}_2}$	$\frac{100\Sigma\text{O}}{\text{N}_2}$	$\frac{100\Sigma\text{H}_2}{\text{N}_2}$
Air	0	53.2	0
1.0	1715	53.3	53.3	1.9
2.5	1010	57.6	57.4	2.3
4.7	860	57.9	59.0	2.7
10.0	738	59.8	62.3	3.0
13.9	660	61.0	65.2	3.3
18.5 (top)	160	64.3	76.1	5.8

The carbon column shows the various ways in which coke charged to the furnace is consumed. For example, the carbon appearing at the 1.0-m level, 53.3 atoms, is the carbon utilized at the bottom of the furnace

in combustion of coke to CO to provide heat and a supply of reducing gas. The increase of 4.3 atoms between the 1.0- and 2.5-m levels corresponds to reduction of solid oxides by carbon. From 2.5 to 10.0 m, the gain is largely caused by evolution of CO_2 from stone; while the increase of 4.5 atoms in the top two sections is carbon consumed by the producer-gas reaction.

Inspection of the oxygen column brings out the relative importance of the various zones in which reduction of the charge is accomplished. For example, the fact that no oxygen is picked up between the tuyeres and the 1.0-m level means that there cannot be any significant reduction of the charge in this region. Neither can there be any appreciable reduction of water vapor in the air. H_2 present at 1.0 m must come from the coke, for otherwise there would be an appearance of oxygen in the shaft gases.

In the carbon-reducing zone (1.0 to 2.5 m) 4.1 atoms of oxygen are removed from the solid charge, while in the CO-reducing zone (10.0 to 18.5 m), oxygen removed amounts to 13.8 atoms. Thus, almost one-quarter of the total reduction is by carbon. Silicon and manganese in the pig cannot possibly account for this amount of reduction by carbon. Neither can it be ascribed to reduction of iron oxide as such, for it is known that Fe_2O_3 , Fe_3O_4 , and FeO are all reducible by CO at relatively low temperatures. The answer must lie in the fact that the charge to this furnace includes quantities of slag. Reduction of FeO chemically combined in slag can be accomplished only by carbon at high temperatures. To return to the upper reduction zone, it is worth noting that most of the reduction by CO appears to take place in the topmost section of the shaft, where 10.9 atoms of oxygen are added to the gas.

The figures in the hydrogen column give evidence of a slow but steady increase in the H_2 content of the gas as it flows up the shaft. Since the total oxygen also increases slowly and the increase may be due to more than one cause, it is impossible to distinguish stoichiometrically between H_2 formed by reaction of water vapor with carbon and residual H_2 distilled from the coke. However, the low percentage of CO_2 reported at the 1.0-m level, together with the fact that H_2O is known to be more easily reduced by carbon than is CO_2 , suggests that water vapor in the air must be almost quantitatively reduced by the time the gases reach the 1.0-m level. If this be true, the absence of any increase of oxygen in the dry gas between the tuyeres and the 1.0-m level indicates that the amount of water vapor in the entering air is negligible and that all the H_2 appearing at higher levels in the shaft is residual H_2 from the coke.

Perhaps the most sensitive test of the data is to focus upon the increments in the total amount of each element, as the gas moves from one sampling point to the next one. In particular, it is instructive to calcu-

late the ratios of the increments of carbon and oxygen. Increments taken from the preceding table are listed below.

Height above tuyeres, m	$t, ^\circ\text{C}$	$\Delta(100\Sigma\text{C}/\text{N}_2)$	$\Delta(100\Sigma\text{O}/\text{N}_2)$	$\Delta(100\Sigma\text{H}_2/\text{N}_2)$	$\Delta(\Sigma\text{O})/\Delta(\Sigma\text{C})$
Air-1.0	-1715	53.3	0.1	1.9	0.002
1.0-2.5	1715-1010	4.4	4.1	0.4	0.93
2.5-4.7	1010-860	0.3	1.6	0.4	5.3
4.7-10.0	860-738	1.9	3.3	0.3	1.7
10.0-13.9	738-660	1.2	2.9	0.3	2.4
13.9-18.5 (top)	660-160	3.3	10.9	2.5	3.3

Several facts about the above figures should be noted. In the first place, the value of 0.93 obtained for $\Delta\text{O}/\Delta\text{C}$ in the 1.0- to 2.5-m section is within 7 per cent of the theoretical value of 1.0, based on the assumption that the principal reaction occurring there is the reduction of solid oxides by carbon. Since reduction by CO goes on at a considerably higher level in the shaft and oxides reduced by carbon but not by CO are known to be reducible only with difficulty at the highest temperatures existing in a blast furnace, it is reasonable to suppose that most of the reduction by carbon is effected in the lower, hotter portion of the 1.0- to 2.5-m section. In the upper portion of this section, there is presumably little chemical reaction of any sort going on.

In the 2.5- to 4.7-m section, the increments of carbon and oxygen are clearly small compared to those in other sections. Here, too, then, there is apparently little chemical reaction occurring, except evolution of final traces of CO_2 from the stone, in the upper part of the section. It can be said that there is an appreciable section of the shaft, extending from about the 1.5-m level to the neighborhood of 4.0 m, in which chemical reaction is negligible and the major activity that is going on is heat transfer between the rising gas and descending charge. Because of the small increments involved in the 2.5- to 4.7-m section, the value of 5.3 for the ratio of $\Delta\text{O}/\Delta\text{C}$ is of low accuracy and not particularly significant.

It has already been pointed out that the principal reaction between the 4.7- and 10.0-m levels appears to be evolution of CO_2 from stone. For this reaction, the theoretical value of $\Delta\text{O}/\Delta\text{C}$ is 2.0, and it can be seen that the value of this ratio for the 4.7- to 10.0-m section agrees with the theoretical within 15%. This is quite satisfactory when one recalls that small errors in the original data are greatly magnified by the taking of differences.

Since reduction of iron oxides by CO affects only the oxygen content of the gas and not the carbon, while the producer-gas reaction affects the carbon content of the gas but not the oxygen, the values of $\Delta\text{O}/\Delta\text{C}$ in the top two sections are equal to the mols of CO reacting with the ore, divided by the mols of CO_2 reacting with carbon.

From the picture of furnace operation given by the shaft-gas analyses, it is possible to estimate the coke consumption, expressed as tons of fuel per ton of pig produced. On a basis of 100 mols of N_2 , the carbon from the coke can be estimated as 53.3 atoms utilized to produce heat and CO, 4.3 atoms to reduce FeO in the open hearth and other slags included in the charge, and 4.5 atoms used in the producer-gas reaction at the top of the shaft, making a total of 62.1 atoms. The oxygen contained in the iron oxides in the charge includes 4.1 from the carbon-reduction zone and 13.8 from the CO-reduction zone, or a total of 17.9. The average state of oxidation of the iron in the mixed charge is not given; but the atomic ratio of iron to oxygen must lie between the extreme limits of 1.0 for FeO and 0.67 for Fe_2O_3 , and the error cannot be very large if an average composition of 0.75, corresponding to Fe_3O_4 , is assumed. From these figures, the ratio of coke to pig is readily calculated. Remembering that the pig is 91% iron and the coke 75% carbon, one finds that this ratio is $\frac{62.1(12)(0.91)}{(0.75)(17.9)(0.75)(56)} = 1.2$ tons of coke per ton of pig. In actual fact, the coke consumed and pig produced by this furnace were measured independently and are reported in the original reference from which Ullmann secured the data on the shaft-gas analyses. The directly measured ratio of coke to pig is 1.1.

The above calculations of the ratio of coke to pig furnish a good check upon the accuracy of the shaft-gas analyses and the way in which they have been interpreted. It has been shown that the data are remarkably self-consistent and give a valuable insight into the processes going on in the reaction vessel. However, a question that merits some discussion is that of the dependability of sampling techniques in the shaft of a blast furnace. Up to this point, the computations have assumed that the gas samples withdrawn at various levels are reasonably representative samples of the total gas stream passing up through the shaft. Is this assumption justified, and if not, how does that fact affect the general reliability of the calculations?

That the sample withdrawn at a given level is truly representative of the gas stream passing through the entire cross section of the furnace at that point is highly unlikely. The fact that the coke and stone are in lump form, while the ore particles are usually relatively small, must lead to segregation and channeling of the solid charge; and this in turn must cause differences in resistance to gas flow, which lead to channeling of the gas. It is also very probable that the flow of solid and gas is much faster at the center of the shaft than it is near the walls.

On the other side of the picture, there are factors tending to minimize the effects of segregation and channeling. For one thing, the solid charge is in motion, and as it moves down the shaft it must undergo a continual process of reshuffling and mixing. A second point is that the history of

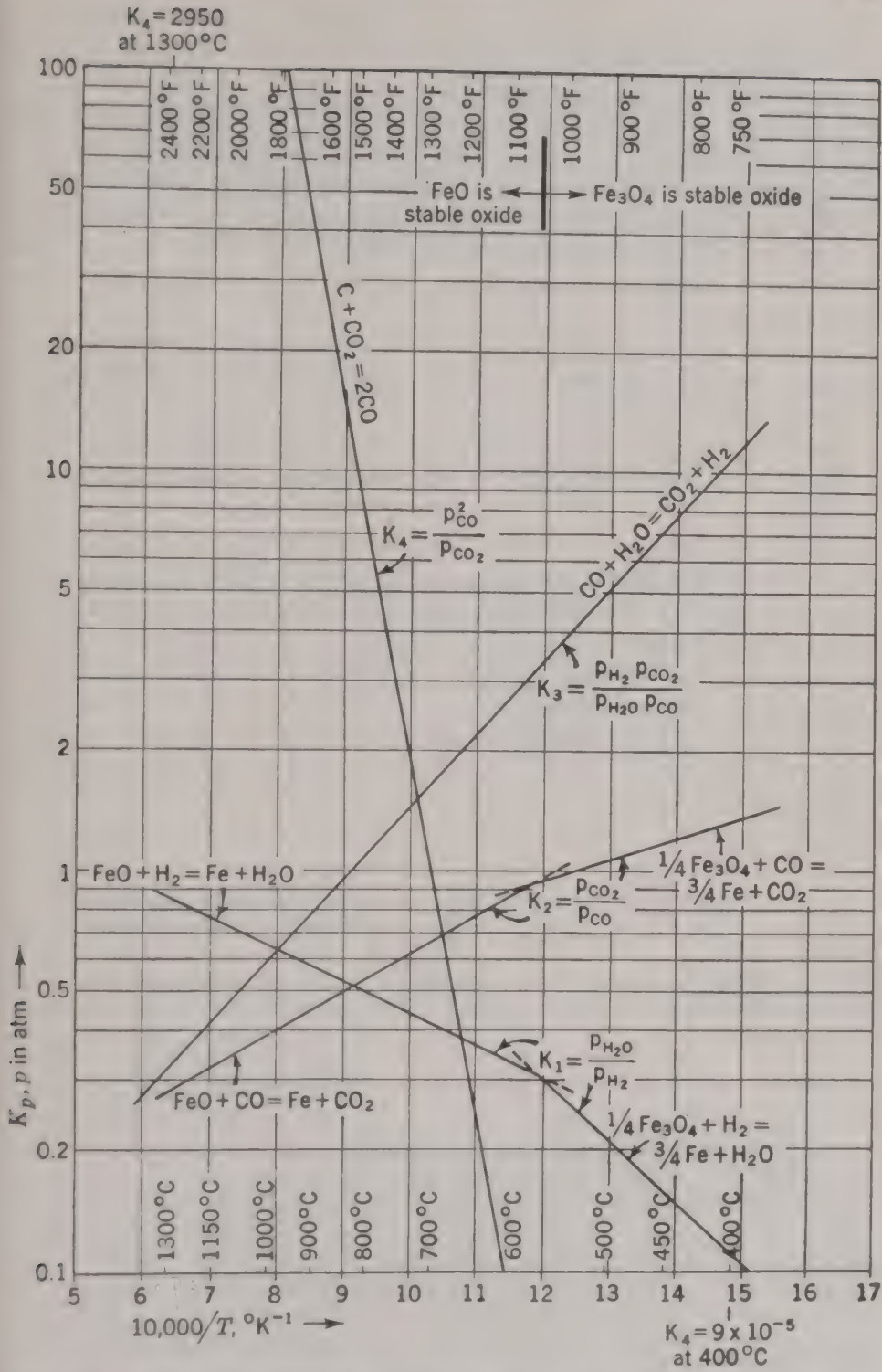


FIG. 10-4. Equilibrium constants of the reduction of iron oxides and carbon dioxide.

each element of gas as it moves up the shaft must be somewhat parallel to the history of all the other elements, although the level in the furnace at which a given stage of reaction is reached may not be the same for each element. In general, it may be said that each of the various gas analyses corresponds to a definite stage in the interaction between ascending gas and descending solid, but that the level from which the sample was withdrawn may not correspond exactly to the level at which the bulk of the gas stream reaches the stage in question. It is obvious that uncertainties are reduced, if gas samples are collected over a long period of time.

Finally, it is of interest to compare the CO and CO₂ in the shaft-gas analyses with (1) equilibrium data on the reduction of iron oxides and (2) equilibrium data on the reaction of CO₂ with carbon. A review of the data on the equilibrium constants for these reactions has been made by Austin and Day.¹ Figure 10-4 is a plot of the values recommended by them.

Perhaps the simplest way to see the relation of actual conditions in the furnace to equilibrium is to compare the actual values of $p_{\text{CO}_2}/p_{\text{CO}}$ and $p_{\text{CO}}^2/p_{\text{CO}_2}$ at each level in the shaft with equilibrium values at the corresponding temperature. The ratio $p_{\text{CO}_2}/p_{\text{CO}}$ is obtained from the gas analyses, as the ratio of per cent CO₂ to per cent CO. In the calculation of $p_{\text{CO}}^2/p_{\text{CO}_2}$, the units of partial pressure do not cancel; and it is necessary to use the data on the total pressure in the shaft to compute p_{CO} and p_{CO_2} . The calculations are tabulated below, and the results are shown in graphical form in Figs. 10-5 and 10-6.

Height above tuyeres, m	Pres- sure, atm abs.	T, °K	$\frac{10,000}{T}$	Per cent CO ₂	Per cent CO	$p_{\text{CO}_2}/p_{\text{CO}}$		$p_{\text{CO}}^2/p_{\text{CO}_2}$	
						Actual value calcu- lated from gas analy- sis	Equi- lib- rium value read from Fig. 10-4	Actual value calcu- lated from gas analy- sis	Equi- lib- rium value read from Fig. 10-4
1.0	1.250	1988	5.03	0.25	34.0	0.0074	0.21*	58	
2.5	1.225	1283	7.78	0.35	35.6	0.0098	0.38	44	170*
4.7	1.150	1133	8.81	1.05	34.9	0.0301	0.48	13.3	21
10.0	1.082	1011	9.88	2.00	34.6	0.0578	0.60	6.49	2.5
13.9	1.038	933	10.71	3.0	34.0	0.0882	0.72	4.00	0.43
18.5	1.0076	433	23.09	7.4	30.3	0.244	1.25	

* Extrapolated values.

¹ J. B. Austin and M. J. Day, *Ind. Eng. Chem.*, 33, 23 (1941).

Figure 10-5 is of interest because of the light it throws on reduction of iron oxides by CO. As would be expected, the composition of the gases moving up the shaft shows a trend toward equilibrium. On the other hand, the approach to equilibrium is not close; and it is evident that nearness to equilibrium is not a serious factor in determining the top-gas composition. If one makes a rough extrapolation of the trend of the gas analyses (the dotted line in Fig. 10-5), the horizontal line corresponding

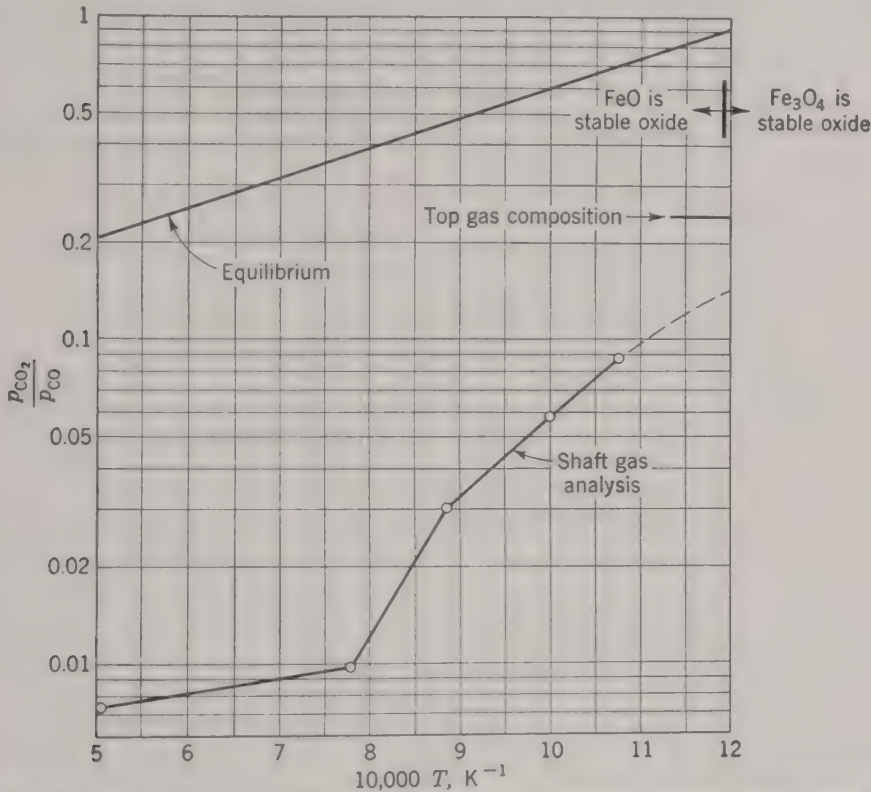


FIG. 10-5. Comparison of blast-furnace shaft-gas analyses with equilibrium of the reaction $FeO + CO = Fe + CO_2$.

to the top gas composition is intersected at a temperature of approximately $500^{\circ}C$. Below this temperature, apparently, there is little if any chemical interaction of charge and gas. At the same time, it has already been shown that most of the reduction of iron oxides occurs in the top section of the shaft; and the highest temperature in this section is $660^{\circ}C$. Therefore, reduction of iron oxides by CO must take place in a relatively narrow temperature range, approximately $500^{\circ}C$ to $700^{\circ}C$.

Interpretation of Fig. 10-6 is not quite so self-evident. According to the graph, the line corresponding to the actual analysis of the gas crosses the equilibrium line at a temperature of about $820^{\circ}C$, and below this temperature the reaction $CO_2 + C = 2CO$ cannot go to the right,

because the equilibrium is unfavorable. This directly contradicts a previous conclusion, which was that the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ must be going to the right in the top section of the shaft, at temperatures not exceeding 660°C . Actually, the most probable explanation seems to be

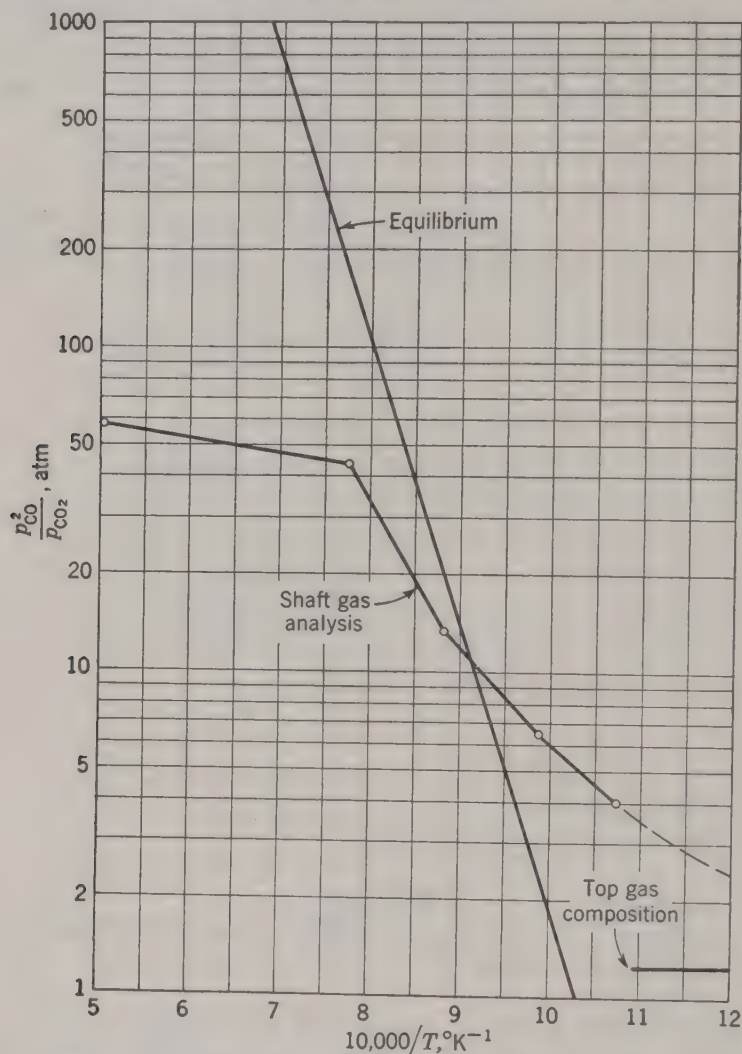


FIG. 10-6. Comparison of blast-furnace shaft-gas analyses with equilibrium of the reaction $\text{C} + \text{CO}_2 = 2\text{CO}$.

that the equilibrium data do not correspond exactly to true conditions of equilibrium in the shaft; for the laboratory data were obtained with carbon in the form of graphite, whereas carbon in the shaft is more or less amorphous in character. There is evidence to indicate that amorphous carbon is a more powerful reducing agent than graphite, particularly at lower temperatures.¹ If this be true, the equilibrium line in Fig. 10-6

¹ *Ibid.*

should be displaced a little to the right, with an increasing degree of displacement at the lower end.

Illustration 4. Assume that tomorrow afternoon you are to attend a staff meeting of a small steel company to discuss performance of their ferromanganese blast furnace. You have been given the following information and average data as representative of their operation, expressed on a 24-hr basis. Production: 93 tons* of pig, averaging 75% Mn, 6% C, and 0.3% Si. (The low silicon is dictated by the use to which the pig is to be put and is obtained by holding a low temperature, around 1420°C, at the tuyere level in the furnace.) Ore charged: 186 tons

Basis: 1 day of operation.

Stream	Tons	Ton atoms			Tons	
		Mn	Fe	C	CaO + MgO	SiO ₂ + Al ₂ O ₃
Input:						
Ore.....	186	1.727	0.233	11.2
Stone.....	94	0.94	52.6
Coke.....	241	16.25	14.5
Air.....	971
Totals.....	1492	1.727	0.233	17.19	52.6	25.7
Output:						
Pig.....	93	1.27	0.312	0.47	(0.3)
Slag.....	107	0.279	40.7	43.8
Dry top gas.....	1240	16.2
Totals.....	1440	1.549	0.312	16.67	40.7	44.1
Differences.....	-52	-0.178	+0.079	-0.52	-11.9	+18.4

In this table the air is $18,700(60)(24)/359(2240) = 33.5$ ton mols = 971 tons. Dry top gas (average mol. wt. 28.3) = $33.5(0.79)/(0.605) = 43.8$ ton mols = 1240 tons. In the total input, moisture in the air is omitted but so is moisture in the top gas, which must include that in the air. The moisture in the coke, 31.3 tons = 1.74 ton mols, should perhaps be added to top gas, which would reduce the differences between total input and output to 21 tons. Moisture in ore and stone could reduce it still further, although some of the H₂ in top gas could be due to moisture decomposition by carbon, in which case that water would show up in dry top gas. Total top-gas hydrogen is equivalent to 26 tons of moisture per day, had it all come from this source. Iron in the pig is assumed by difference, 18.7%. Because of incomplete data, lime and magnesia are lumped together, and likewise silica and alumina. The stone is treated in the table as pure CaCO₃. The equivalent of silicon in the pig is shown in the last column in parentheses (its oxygen went off in top gas).

* All tons are long tons (2240 lb).

(51% Mn, mainly as slightly hydrated dioxide, 7% Fe, and 6% SiO_2). Stone: 94 tons. Coke: 241 tons (81% C and 13% moisture). Slag: 107 tons (about 37% CaO , 1% MgO , 12% Al_2O_3 , 29% SiO_2 , and 18.5% MnO). Blast: 18,700 cu ft/min (d.s.c.). Its temperature entering the tuyeres is 520°C . Top gas averages 6.4% CO_2 , 30.2% CO , 0.4% CH_4 , 2.5% H_2 , and 60.5% N_2 at 515°C . Analyze these data to prepare yourself to participate as constructively as possible in the conference.

Discussion. The table on page 351 is largely self-evident, but certain details of its computation are given below it.

Looking at these balances, one is at first inclined to think that the check of total input and output seems excellent, particularly in view of the fact that output should be increased by an amount of moisture that might be over 30 tons. On second thought, however, one realizes that, since the amount of top gas was calculated from the amount of inlet air by a nitrogen balance, the quantity of that air, 971 tons, merely appears on both sides of the balance sheet, even though camouflaged on the output side. The significant items to compare would be input and output, both less air; *i.e.*, $\text{input} = 1492 - 971 = 521$ tons, and

$$\text{output} = 1440 - 971 = 469 \text{ tons}$$

The discrepancy is 10% and will be discussed further below.

As to the element balances, the manganese deficiency is also about 10%. This may well be ore dust blown over in the top gas; if so, it needs no discussion, since methods of handling it are obvious. The loss in the slag is serious, but it too will be considered later. The iron discrepancy is high, 34% of the input figure, but the per cent in the pig is high, obtained as it was by difference, and the iron in the ore is a rounded figure, which might easily be low. Moreover, iron is a small item in the total figures. The carbon balance looks excellent. Another check can be obtained by a balance on oxygen other than from air. Manganese in the pig gave up $1.27(2) = 2.54$ atoms; that in the slag, 0.279 atom. The iron in the pig lost $0.312(1.5) = 0.47$ atom, the silicon 0.02, and the CaCO_3 , $0.94(2) = 1.88$, totaling 5.19 atoms of oxygen lost by the burden to the gas. The total oxygen in the top gas less that equivalent to its nitrogen is 10.84 atoms per 100 mols dry gas, or 4.75 atoms per day, a deficiency of 8.5%. On the whole, while the data are not exact, their general consistency is sufficient to justify careful study of them till more dependable figures are available.

As to the slag-forming components, it is striking that $\text{CaO} + \text{MgO}$ show a 23% deficiency whereas $\text{SiO}_2 + \text{Al}_2\text{O}_3$ have a 72% excess. The sum of the two quantities, 6.5 tons, is only 6% of the total slag. However, the input figures *assumed* the stone to be pure CaCO_3 . If one will calculate the CaCO_3 in the stone used as equivalent to the CaO in

the slag, $107(0.37) = 39.6$ tons, or 0.706 ton mol, and assume the rest of it, $94 - 70.6 = 23.4$ tons, to be $\text{SiO}_2 + \text{Al}_2\text{O}_3$, the balances look far better. $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ input becomes $25.7 + 23.4 = 49.1$ tons vs. an output of 44.1, or an excess of 5.0 tons. The $\text{CaO} + \text{MgO}$ now show the magnesia only as excess, 1% of 107 tons of slag, or 1.1 tons. The total excess of these slag-forming components is 6.1 tons, less than 6% of the total slag. Meanwhile, this also makes the carbon input drop by 0.23 atom to a total of 16.96 atoms vs. the output of 16.67, or a deficiency of less than 2%. Moreover, the oxygen input from the burden drops to $5.19 - 2(0.234) = 4.72$, compared with the 4.75 showing up in the top gas. This leads to the conclusion that substantially all the moisture in the burden went off as such in the top gas and should have been added to total output, greatly reducing its discrepancy. The conclusion seems warranted that the stone used was high in impurities, probably argillaceous.

One is at last in a position to begin to grasp what the figures indicate. The disturbing fact is the manganese loss in the slag, 21% of the product and over 15% of the input. It is extremely improbable that the slag analysis for manganese is significantly in error. The loss is real. The question is, what can be done about it?

There are two possible explanations of the high concentration of manganese in the slag. It may be that insufficient time has been provided in the bottom of the furnace for the reduction of the manganese out of the slag, or it may be that the reducing conditions in the bottom of the furnace are inadequate for removal of the metal from the slag, *i.e.*, that the slag is essentially in manganese equilibrium with the metal.

Were the charge to the furnace pure MnO and carbon only, the cause of incomplete reduction would indeed be inadequate time for reaction. One would be dealing with a three-component system (Mn-O-C) with four phases (metal, carbon, gas, and any unreduced oxide). Having fixed a pressure of operation for this monovariant system, one has fixed all phase-rule variables. Paraphrased, this means that if conditions are such that any reduction at all occurs (*i.e.*, one is not at equilibrium), reduction will keep on going as long as the same conditions are maintained until the oxide has disappeared, *i.e.*, till reduction is complete. However, in the actual furnace there are slag-forming components and the slag is a powerful solvent for MnO . As the MnO content of the slag drops, the difficulty of further reduction of metal from it increases greatly, both from an equilibrium point of view and a rate point of view.

The slag melts in the lower part of the furnace and promptly dissolves a large quantity of the MnO . It flows in relatively thin layers down the shaft of the furnace, over the lumps of coke that fill it. When it reaches the crucible and accumulates in a pool, there is submerged in it a pile of

solid hunks of coke, held down in it (and in the pig as well) by the weight of the furnace burden. This means that the slag has had extensive contact with solid carbon, but whether this has been sufficient to carry reduction to substantial equilibrium is not clear.¹

If more time is required to complete reduction, one solution would be to carry a much deeper layer of slag above the pig in the crucible of the furnace, thereby increasing its residence time and its contact with solid carbon. Another approach might be to increase reduction rate by increasing crucible temperature and perhaps also by modification of slag composition. However, in a given furnace producing a product of satisfactory quality, one always hesitates to tamper with either of these two factors.

Assume for the moment that the slag has indeed come to substantial Mn equilibrium with the pig, so that further time of contact with carbon will achieve no further reduction. It follows that the manganese loss in the slag is proportional to the amount of the slag, since the percentage of manganese in the slag is dictated only by the conditions of equilibrium. Now the function of the slag is to get rid of the unreducible impurities in the charge, and hence its quantity ought to be proportional to those impurities. These contaminants are the gangue of the ore and the ash of the coke, the amounts of which can probably not be reduced in a case like this. These impurities, however, are predominantly siliceous and argillaceous; they are infusible or impossible to handle by themselves under furnace conditions. They must be fluxed by conversion to metallic silicates and aluminates by addition of lime in suitable proportion. The trouble in this furnace is that the lime itself carries an excessive amount of silica and alumina. Indeed, roughly half the total $\text{SiO}_2 + \text{Al}_2\text{O}_3$ charged to the furnace comes from the stone. If one can get pure CaCO_3 as flux, the amount of slag and therefore also the manganese loss in the slag can immediately be reduced one-half by this step alone, with no change whatever in furnace conditions at the crucible, either as to temperature or as to the composition of pig or slag. Indeed, if one wishes, the total average slag quantity in the crucible can be kept unchanged simply by allowing it twice the residence time in the crucible. Meanwhile, the quantity of the purer stone required would be only about 35 tons, in contrast to the 94 tons now used. If one can get a 10% increase in ferromanganese production by cutting losses, together with a 63% reduction in stone consumption, along with a minor saving in coke

¹ Conditions in the iron blast furnace differ drastically, in that iron ore is reduced by CO in a zone in the furnace shaft above that at which slag melts. MnO, however, is harder to reduce, requiring a higher temperature than iron oxide. The amount of surface in direct contact with solid carbon is also an important factor in determining the rate of reduction of either oxide.

due to lowered heat requirement, all with no new investment and no increase in total operating expense whatever, one can well afford to pay a far higher price per ton for the better stone. This assumes no possible further reduction from the slag; if more reduction can indeed be achieved, the argument still holds, but in progressively lessening degree. The first thing to do is to find out if the stone is indeed as impure as the data indicate. The second is to explore the possibility and practicability of further reduction of metal from the slag.

Still another possibility would be to put the high-manganese slag through a small auxiliary coke-reduction furnace, operated at far higher temperature, to recover most of the manganese as metal. Reduction could be aided by making the slag much more basic in this step. The product would be impure but could be returned to the main furnace for what would be essentially a refining operation by recycling. However, no such suggestion should be considered until the potentialities of lessening the quantity of slag and increasing its reduction have been fully explored.

PROBLEMS

1. A blast furnace is charged with 1282 long tons/day of a hematite ore containing 52% iron, 162 long tons/day of limestone containing 53.2% CaO and 1.2% MgO, and 617 long tons/day of coke containing 1.5% iron and 87% carbon. The average analysis of the blast-furnace gas is 11.2% CO₂, 27.4% CO, 2.2% H₂, 0.7% CH₄, and 58.5% N₂. Calculate the following:

(a) The percentage of the total oxygen in the dry blast-furnace gas that comes from reduction of the ore.

(b) The percentage of the total coke gasified in the furnace that is burnt at the tuyeres.

2. A blast furnace was tested over a 24-hr period of steady operation by students at the Buffalo station of the M.I.T. School of Chemical Engineering Practice. The furnace was using a Lake Superior hematite ore carrying 50.5% Fe. The rest of the charge consisted of 690 long tons of coke analyzing 0.3% moisture, 2.0% volatile matter, 85.8% fixed carbon, and 11.9% ash, and 220 long tons of limestone containing 96.0% CaCO₃ and 2.5% MgCO₃. The furnace produced 710 long tons of pig with an average analysis of 1% Si, 1% Mn, 3.7% C, and traces of S and P; 35 long tons of flue dust, carrying 7.0% C, were collected. The average outdoor temperature was 74°F and the blast entered the tuyeres at 1120°F and 22 psig. The average analysis of the top gas was 11.1% CO₂, 26.1% CO, 1.2% CH₄, 3.9% H₂, and 57.7% N₂.

(a) Estimate what per cent of the total oxygen in the dry top gas came from the ore and what per cent from the stone.

(b) How much air is delivered by the blowing engines to the tuyeres, in cubic feet per hour at 32°F and 760 mm Hg abs?

(c) Of the total heat above atmospheric temperature supplied to the base of the furnace, estimate what per cent was supplied as sensible heat in the air and what per cent as heat due to combustion of carbon burnt at the tuyere level.

(d) Express and explain your opinion as to the general dependability of the data.

3. The following data are totals or averages, as the case may be, from the record sheet of a blast furnace for a 24-hr period (midnight to midnight) during which the

operation was extremely steady. All weights are in long tons. The charge consisted of 2028 tons of hematite ore (53.1% Fe), 168 tons of open-hearth slag (21.2% Fe), 60 tons of flue dust (7.2% coke), 958 tons of coke (84% C), and 337 tons of stone (94.7% CaCO_3). The production of pig was 1236 tons, and its average analysis 0.047% S, 0.89% Si, 0.64% Mn, and 4.96% C. The weight ratio of CaO to SiO_2 in the slag was 1.18. The average analysis of the top gas was 13.2% CO_2 , 26.0% CO, 2.5% H_2 , 0.4% CH_4 , and 57.9% N_2 . The temperature of the air intake to the blowers was 60°F, the partial pressure of water vapor in the air 10.7 mm Hg, and the barometer 748 mm. From the total strokes of the blowing engines and their known piston displacement and efficiency, the air delivered to the stoves was calculated to be 4339 tons, moisture-free. What conclusions do you draw from these data as to the operation of the furnace?

4. The equilibrium constant of the reaction $\frac{1}{4}\text{Fe}_3\text{O}_4 + \text{CO} = \frac{3}{4}\text{Fe} + \text{CO}_2$ is equal to 0.77 at 700°C, 0.62 at 900°C, and 0.58 at 1100°C. The constant of the reaction $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$ is 1.80 at 400°C and 1.18 at 500°C. With the aid of this information and Fig. 10-4 determine at several temperatures in the range from 400 to 1100°C the ratio of CO to $\text{CO} + \text{CO}_2$ required for each of the following reactions:

- (a) Reduction of Fe_3O_4 to Fe.
- (b) Reduction of FeO to Fe.
- (c) Reduction of Fe_3O_4 to FeO.

Plot the three ratios versus temperature on a single plot with the temperature in degrees centigrade as the abscissa.

5. A company has available from one of its operations a moderate quantity of pure hydrogen, and it is considering the production of iron for powder metallurgy by reduction of Fe_3O_4 . This is to be done by passing hydrogen up through a bed of Fe_3O_4 moving downward through a cylindrical shaft. Provision will be made for controlling the temperature, and the temperature may be assumed to be constant throughout the bed. The shaft will be equipped with devices to prevent back-mixing of the gas, so that the flow of gas and solids will be essentially countercurrent. No attempt will be made to recycle hydrogen. Laboratory experiments have shown that reduction proceeds rapidly at temperatures of 800°C and above. The question of what is the best temperature at which to operate is being discussed, and you have been asked to determine the influence of temperature on hydrogen requirements. On the assumption that the shaft will be high enough so that chemical equilibrium is closely approached, calculate the mols of H_2 required per atom of Fe produced at 800 and 1300°C.

6. In the reduction of zinc oxide with carbon in a conventional retort at atmospheric pressure three main reactions are involved. At temperatures of 600 to 700°C and above, the reaction $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$ is rapid. At 900 to 1100°C ZnO reacts with carbon to form Zn and CO. At 1100 to 1300°C, the range of temperature in which the bulk of the distillation is normally conducted, the rate of reduction of CO_2 by carbon is appreciable. At no stage in the operation is it desirable to have any significant amount of CO_2 in the exit gases, since as the gases are cooled, the reaction $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$ reverses and a portion of the zinc vapors is reoxidized. To suppress formation of CO_2 the usual practice is to provide a large excess of carbon in the original charge, so that the gas phase in the retort is in contact mainly with carbon, and to heat the charge as quickly as possible to temperatures at which the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ is rapid. Despite these precautions a certain fraction of the zinc vapors is always reoxidized. Furthermore, the large excess of carbon reduces the amount of ZnO that can be included in the charge to a retort and hence reduces its production capacity.

Values of the equilibrium constant of the reaction $\text{ZnO} + \text{CO} = \text{Zn(gas)} + \text{CO}_2$ have been reported by Maier,¹ as follows:

Temperature, °C	$p_{\text{Zn}}p_{\text{CO}_2}/p_{\text{CO}}$, partial pressures in atmospheres
627	1.970×10^{-5}
727	2.416×10^{-4}
827	1.849×10^{-3}
927	9.943×10^{-3}
1027	4.088×10^{-2}
1127	1.362×10^{-1}
1227	3.845×10^{-1}

(a) If an ordinary tight retort is charged with zinc oxide and excess carbon and the gases are vented as heating proceeds in order to maintain essentially atmospheric pressure within the retort, and if the rate at which the zinc is driven off is not a consideration, what is the minimum temperature to which the retort must be heated, if all the metal is to be distilled?

(b) As one possible alternative to providing a large excess of carbon, the use of a retort capable of withstanding pressure has been suggested. If the gases leave the retort at an average temperature of 1100°C, containing not more than 1% CO_2 , and are substantially at equilibrium so far as interaction of ZnO and CO is concerned, but not with respect to reduction of CO_2 by carbon, what pressure must be held on the retort?

7. The table below shows analyses of the gases leaving a Bessemer pig-iron converter at various times after the beginning of the blow.² The total length of the blow in question was 18 min.

Gas	Time from commencement of blow, min					
	2	4	6	10	12	14
CO , %.....	nil	3.95	4.60	19.59	29.44	31.11
CO_2 , %.....	10.71	8.57	8.15	3.58	2.39	1.34
O_2 , %.....	0.92					
N_2 , %.....	88.37	{ 86.58	{ 85.25	76.83	{ 66.01	67.55
H_2 , %.....		{ 0.88	{ 2.00		{ 2.16	

What are your conclusions from these data?

8. The U.S. Bureau of Mines tested a blast furnace in South Chicago, Ill., to determine the composition of the gas at various levels in the shaft.³ The greater part of the burden in this furnace consisted of hematite ores from the Mesabi Range. The average gas compositions tabulated below were obtained by the most careful methods of sampling and analysis.

¹ C. G. Maier, *U.S. Bur. Mines Bull.* 324 (1930).

² J. Snelus, *Iron Steel Inst.* II, 247 (1871). Quoted by C. R. Alder Wright in the article on Iron, "Encyclopaedia Britannica," 9th ed. (1881).

³ S. P. Kinney, *U.S. Bur. Mines Tech. Paper* 442 (1929).

Location	Distance above tuyeres		Average per cent				Temperature, °F	Pressure, in. Hg gauge
	Feet	Inches	CO ₂	CO	H ₂	N ₂		
Blast.....	1,138.0	39.1
Tuyeres....	0	0	0	32.0	1.37	66.63	2,372.0	30.6
Plane 4....	24	0 $\frac{1}{4}$	5.5	34.7	0.9	58.9	1,727.5	22.7
Plane 3....	46	6 $\frac{1}{4}$	11.9	27.7	2.3	58.1	1,574.6	13.22
Plane 2....	57	1 $\frac{1}{4}$	15.2	25.3	3.2	56.3	1,301.0	10.31
Plane 1....	65	1 $\frac{1}{4}$	14.9	25.2	3.4	56.5	724.7	4.74
Top.....	68	1 $\frac{1}{4}$	14.7	24.8	4.1	56.4	400	3.98

The air supply at the time of the test was 828.9 cu ft/sec at 32°F and 29.9 in. Hg, and it carried 5.37 grains of H₂O per cubic foot. The output of the furnace was not measured at the time the above data were obtained, but plant records indicated that the normal production was approximately 700 long tons of pig iron per day. Check the accuracy of the test data by computing the daily production of pig iron in long tons from the reported air rate and gas compositions. In the light of the results, what is your judgment as to the dependability of the test data? What do they indicate regarding operation of the furnace?

9. A zinc smelter operated by the St. Joseph Lead Company¹ uses a zinc sulfide concentrate as raw material. The sulfide concentrate is first roasted. The roasted concentrate is mixed with the "blue powder" (see below) and a portion of the residue from the smelting furnace and is then sintered. The sinter is mixed with coke, and the mixture is preheated to 850°C in a rotary furnace fired with a portion of the waste gases from the water washer attached to the smelting furnace. Volatilization of zinc in the preheater is negligible. The preheated mixture is charged to a continuous smelting furnace. The average analyses of the dry sulfide concentrate, roasted concentrate, and sinter are tabulated below:

Constituent	Zinc sulfide concentrate	Roasted concentrate	Sinter
Zn.....	58.28	67.69	58.94
Pb.....	0.56	0.06	0.03
Insolubles.....	1.6	1.75	9.48
SiO ₂	1.12	1.26	8.62
Fe.....	6.4	7.24	9.02
Al ₂ O ₃	1.3
CaO.....	0.47	0.47	1.1
MgO.....	0.27	0.36	0.6
Mn.....	0.24	0.27	0.39
Cu.....	0.06	0.07	0.11
Cd.....	0.1	0.1	0.005
S.....	31.9	1.88	0.23
Loss on ignition.....	1.1

¹ G. F. Weaton and C. C. Long, *Metals Technol.* 6 (February, 1939).

The coke contains 0.6% volatile matter, 86.6% fixed carbon, 12.8% ash, 0.018% Cl, and 0.94% S.

The smelting furnace is 37 ft high with an internal diameter of 69 in. and is of the charge-resistor type. The electrodes, which are of pitch-impregnated carbon, are consumed at the rate of 5 lb per short ton of zinc produced. Sinter and coke are charged to the top of the furnace at the rates of 36 lb/min and 16 lb/min, respectively. The main body of the solids in the furnace shaft is at a temperature in the neighborhood of 1200°C. As the charge moves down the shaft, 70 to 73% of the ZnO in the sinter is eliminated. The furnace residue is withdrawn at the bottom of the shaft, and the ash and unused coke are separated. The remaining residue is divided, a portion being discarded and the rest mixed with the roasted concentrate, as noted above. The vapors leave at 850°C through the side of the furnace, which operates under a slight vacuum.

From the furnace the vapors pass to a condenser in which most of the zinc is condensed and removed from the system. The condensate removed at this point is the plant product and contains less than 0.007% Fe and 0.025% Pb. The uncondensed vapors leave the condenser at 550°C and flow to a water washer in which the gases are cooled to atmospheric temperature and zinc is precipitated as "blue powder." Both the condenser and washer are under a vacuum of 16 to 18 in. Hg. At the location of the smelter the average barometer is 29.2 in. Hg. The gases leaving the washer analyze 82% CO, 1.6% CO₂, 1.4% O₂, and 15% N₂. The over-all recovery of zinc from the sulfide concentrate averages 92.62%.

- (a) Estimate the percentage of the zinc in the blue powder that is present as oxide.
- (b) Identify the point or points in this plant at which the chief losses of zinc are occurring, and determine what percentage of the total loss of zinc is being lost at each point. Can you suggest any steps that might be taken to improve over-all recovery?
- (c) What percentage of the furnace residue (after removal of ash and coke) is recycled?
- (d) Compute the daily production of liquid zinc in short tons.

10. The input of electrical energy to the furnace of Prob. 9 is 2564 kwhr per short ton of zinc produced. What fraction of this energy is lost as heat through the walls?

11. Analyze the performance of the ferromanganese blast furnace of Illustration 4 from the standpoint of the utilization of energy. What are your conclusions and recommendations?

Chapter 11

CERAMICS

Computations in the field of ceramic technology will naturally include those pertaining to combustion operations and to related problems having to do with the design of furnaces and kilns. Computations of this sort are covered in Chaps. 2 through 5 and in Chap. 12. Additional problems will involve the ware itself, particularly the estimation of the amounts of raw materials required to produce a body, a glaze, or an enamel of a desired composition. Problems of this type are the subject of this chapter.

The chemical compounds in the raw materials used by the ceramic industries are extremely complex, and in many cases their exact constitutions are unknown. Most materials are relatively impure in the usual chemical sense, and they may consist of several chemical compounds of indefinite composition, sometimes in varying proportions. However, methods have been developed to simplify the calculations required and to rationalize the complex constitution of raw materials and of ceramic compositions made from them so that they may be treated as conveniently as if they were simple, pure chemical compounds, or at least no more complex than industrial gas mixtures such as have already been treated in other chapters.

For example, the mineral kaolinite has the chemical formula $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$, which shows that it is an aluminosilicic acid containing the designated number of hydrogen, aluminum, silicon, and oxygen atoms. For purposes of calculation, however, the formula is more conveniently written in terms of the constituent oxides, as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, as this formula shows that kaolinite may be treated stoichiometrically as if it consisted of a mixture of 1 mol of alumina, 2 mols of silica, and 2 mols of combined water. Similarly, the mineral orthoclase (potash feldspar) is written as $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ rather than as $\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$, or as KAlSi_3O_8 .

Empirical formulas. The ceramic industries, however, do not use pure kaolinite and pure orthoclase but use clay (kaolin) and commercially available feldspar. The latter usually contains sodium oxide and possibly calcium and magnesium oxides in place of part of the potassium oxide,

and the ratios of alumina and of silica to basic oxides may differ from the exact 1:1 and 6:1 ratios, respectively, as specified by the formula for orthoclase. However, the raw material from any given source will have a reasonably uniform chemical analysis, from which the proportions of the oxides may be computed. The composition may then be expressed as an empirical formula similar to the exact chemical formulas shown above for pure materials.

In writing empirical formulas, the oxides are arranged in the order $R_2O, RO \cdot R_2O_3 \cdot RO_2$. R denotes any element of the proper valence to correspond with the formula for the oxide in which it appears. Thus, R_2O stands for K_2O or Na_2O ; RO for the alkaline-earth oxides, or for zinc or lead oxides; R_2O_3 for Al_2O_3 ; RO_2 for SiO_2 ; etc. To further simplify the writing of a formula for a general type of composition, ceramists commonly use RO to denote all basic, or fluxing, oxides. The actual formula will disclose whether K_2O , Na_2O , CaO , ZnO , or other oxide is meant.

Illustration 1. The analysis of a New York State feldspar has been found to be as follows:

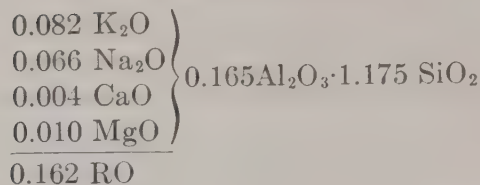
	<i>Per cent</i>
SiO_2	70.60
Al_2O_3	16.80
CaO	0.25
MgO	0.39
K_2O	7.70
Na_2O	4.06

Calculate the empirical formula and formula weight from this analysis.

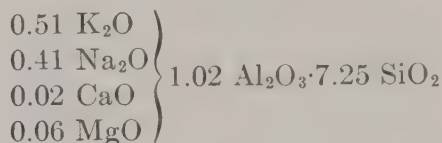
Solution. Take as a basis for calculation 100 parts by weight of the feldspar and compute the number of mols of each constituent oxide.

Oxide	Parts by weight	Mol. weight	Mols
SiO_2	70.60	60	1.175
Al_2O_3	16.80	102	0.165
CaO	0.25	56	0.004
MgO	0.39	40.3	0.010
K_2O	7.70	94	0.082
Na_2O	4.06	62	0.066
Total.....	99.80		

These results are then arranged in the order $R_2O, RO \cdot R_2O_3 \cdot RO_2$ as follows:



To make the RO group add up to unity, all terms are then divided by 0.162, giving



Since 100 lb of feldspar (99.8 lb accounted for in the analysis) contain 0.162 formula weights (basis RO = unity), the formula weight must be $100/0.162 = 617$. Note that this is not $99.8/0.162$. Although the difference would be negligible in this case, a large error would result for a substance like clay or whiting in which there is a large amount of volatile matter that is neglected in deriving the empirical formula in terms of nonvolatile oxides. Thus, 617 is the "formula weight" since it is the number of pounds, or other weight units, that must be taken to obtain one unit of the "formula" as written, but it includes the 0.2% of "unaccounted-for" material, which may be "loss on ignition" or, what is more probable, the accumulation of all the errors in the analysis for the individual elements.

Fractions of molecules do not exist; thus, 617 is not the "molecular weight" in the usual chemical sense in which these terms are used. However, the "formula" will be considered as being made up of so many "mols" of individual oxides or other groups, so that the term "mol" has the same significance here that it has in other chapters.

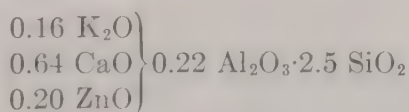
The ratio of Al_2O_3 in this spar to RO is seen to be nearly 1:1, but the ratio of SiO_2 to RO is 7.25:1. Since the highest ratio of SiO_2 to RO in aluminosilicates of definite chemical composition is found in orthoclase or albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), the ratio of 7.25 indicates that some free quartz is associated with the aluminosilicates.

Formulation of ceramic mixes. Empirical formulas are convenient in making computations for ceramic mixes, they facilitate making comparisons between one formula and another, and they aid in visualizing the effect of differences in composition that are not readily discernible from a weight analysis. There is some scientific basis for this last advantage. Most ceramic wares are heated to the point where there is more or less fusion of the various constituent materials. Thus, the fusion point or vitrifying point is an important physical property. Vitrification is aided by the fluxing oxides, K_2O , Na_2O , and others of the

RO group. On a weight basis these oxides are not equivalent, pound for pound, in their effect on fusion point, but on a molecular basis 1 mol of one oxide comes much closer to substituting for 1 mol of another oxide of the same class. As with aqueous solutions the correspondence between fusing point and composition is reasonably close so long as the solution is dilute (up to 1 or 2 mol per cent) whatever the molecular species of the solute, but this correspondence cannot be expected to hold for concentrated solutions. Substitution of 0.3 mol of PbO for 0.3 mol of CaO in one formula weight of a glaze would be expected to change the fusing point considerably.

Not all oxides should be placed in the empirical formula according to the valence of the element forming the oxide. To do this would be misleading if it were construed as implying similar chemical behavior to all oxides of like chemical constitution. Thus, FeO belongs with the RO group since it is a basic oxide, but Fe₂O₃ does not behave chemically like alumina even though for practical purposes it may be listed in the R₂O₃ group. Borax yields B₂O₃, which behaves as an acidic oxide like silica, and therefore it should be placed in the RO₂ group rather than with Al₂O₃. Titanium, zirconium, and tin, like silicon, are in Group IV of the periodic table and form oxides having the formula RO₂. These oxides are employed as opacifying agents in glazes. Since they dissolve sparingly at the relatively low temperature at which glazes are fired, they do not enter into reaction with the RO and R₂O₃ groups, and for this reason they are listed separately. Fluorine is another opacifying agent, which is introduced by use of fluorspar or cryolite, and many compositions show this by writing the element by itself or with the RO₂ group. It is preferable to show it with the element with which it is combined originally, such as Na₂F₂, CaF₂, or Al₂F₆. Pigmentary oxides like CoO, which are added in very small amount, are often listed separately. In spite of these limitations, the method of expressing the composition of raw materials, bodies, glazes, and enamels in molal units according to oxide groups is informative and convenient.

Illustration 2. A satisfactory glaze for sanitary ware is stated to have the composition



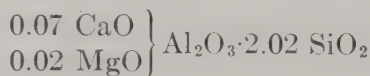
It is desired to find the proportions of clay, feldspar, whiting, and zinc oxide to make this glaze. The analysis of the clay is 44.7% SiO₂, 37.5% Al₂O₃, 1.5% CaO, and 0.3% MgO, the remainder being H₂O and loss on ignition plus cumulative errors. The feldspar has the composition given in Illustration 1. The other materials may be considered practically pure.

Solution. The compositions of the glaze and of the feldspar are available as empirical formulas; other compositions are given in terms of percentages by weight. Calculations may be made either in terms of molal units or in weight units by conversion of all analyses to one basis or to the other. It is seen, however, that the raw materials contain soda and magnesia which are not present in the glaze formula, and this fact might lead one to reject these materials except that a certain amount of substitution of soda for potash and of magnesia for lime is permissible. Thus, it will be preferable to make the computations on a molal basis, as the degree of substitution of one oxide for another will be more clearly apparent. It is, of course, not certain that the composition to be computed when using these materials will yield a glaze of the exact physical characteristics required to go with a particular body. Experimental evidence may be necessary to determine the suitability of the formula.

As a first step, calculate the empirical formula and formula weight for the clay. Basis of calculation is 100 lb of material. Dividing the

Oxide	Pounds	Mol. weight	Mols
SiO ₂	44.7	60	0.745
Al ₂ O ₃	37.5	102	0.368
CaO.....	1.5	56	0.027
MgO.....	0.3	40.3	0.007

mols of each oxide by 0.368 to make Al₂O₃ equal to 1.0 for clay, the empirical formula can then be written as



Similarly the formula weight is $100/0.368 = 272$.

If the amount of each material needed is designated as an unknown quantity, a series of material balances can then be written. Solution of these equations gives the answer to the problem. However, in most problems of this type it is not necessary to resort to an algebraic method, as the amount of some materials is obvious from inspection of the glaze formula. Starting with the more complex materials like feldspar and clay, the amounts of oxides introduced by known quantities of these materials are "checked off" and the remainders needed are supplied by the simple materials like whiting, zinc oxide, and quartz.

To solve the problem by this method, first write down the formula for the glaze in columnar arrangement. It is seen that all the 0.16 mol of R₂O is derived from the feldspar. By simple ratio the number of

formula weights of feldspar needed is $0.16/0.92 = 0.174$ inasmuch as there is 0.92 "mol" of R_2O in the feldspar empirical formula. Below the formula for the glaze, write in the appropriate column the mols of each oxide introduced by this amount of feldspar. Subtracting shows

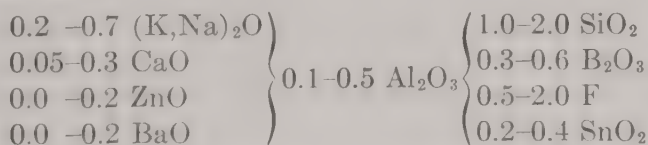
Material	Formula weights	R_2O	RO	ZnO	Al_2O_3	SiO_2	Formula weight	Pounds
Glaze.....		0.16	0.64	0.20	0.22	2.50		
Feldspar.....	0.174	0.16	0.014	0.177	1.26	617	107.4
First remainder.....		0.0	0.626	0.20	0.043	1.24		
Clay.....	0.043	0.003	0.043	0.087	272	11.7
Second remainder.....		0.623	0.20	0.0	1.153		
Whiting.....	0.623	0.623	100	62.3
Zinc oxide.....	0.20	0.20	81.4	16.3
Quartz.....	1.153	1.153	60	69.2
		0.0	0.0	0.0	0.0	0.0		266.9

how much of the other oxides is still needed.

Since all the remaining alumina comes from the clay, the amount of the latter can be written as 0.043 formula weight. The quantities of RO, Al_2O_3 , and SiO_2 introduced by this amount of clay can then be computed. Subtraction gives the second remainder, from which the amounts of whiting, zinc oxide, and quartz are obvious.

The last two columns in the table give, respectively, the formula weight and the number of pounds of material corresponding to the number of formula weights given in column 2. The sum of the figures in the last column is 266.9 lb, which is the "batch weight" for the glaze.

Illustration 3. White enamel for sheet steel can be made by the following formula:



Calculate the batch weight of materials needed to make this formula.

Discussion. Enamels are made from the following ingredients: feldspar, flint, borax, soda ash, niter, fluorspar, cryolite, tin oxide, zinc oxide, manganese dioxide, cobalt oxide, lime or whiting, barium carbonate, red lead, litharge, and other suitable materials.

Examination of the enamel formula shows that an extremely wide variation in composition is permissible and that literally hundreds of different mixes are possible. The formula can be simplified by consideration of the following points:

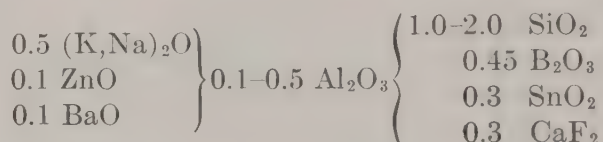
1. Fluorine is probably introduced by fluorspar, which may be indicated by writing it as CaF_2 . As this is an opacifier, it is preferable to list it with SnO_2 , which is used for the same purpose. The equivalent amount of CaO must, of course, be deducted from CaO in the RO group.

2. It is desirable to decide on an average composition that falls within the limits specified in the formula. This is most easily done by fixing the proportions of the oxides in the RO group and of other key materials like B_2O_3 and SnO_2 and letting Al_2O_3 and SiO_2 remain as variables.

3. The formula does not disclose whether 0 to 0.2 mol of ZnO is needed in addition to 0 to 0.2 mol BaO or whether up to 0.2 mol of either oxide is satisfactory. For purposes of illustration it will be assumed that 0.1 mol of each is desired.

4. Because a considerable range in composition is allowable, it will be unnecessary to take into account variations in purity of the raw materials. All of them may be assumed to be pure minerals or chemicals.

Solution. Assume that the following average formula meets with requirements:



By inspection it can be seen that 0.1 mol ZnO , 0.1 mol BaCO_3 , 0.22 mol $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 0.3 mol SnO_2 , and 0.3 mol CaF_2 are needed. Furthermore, the borax used will supply 0.22 mol of Na_2O , leaving 0.28 mol of R_2O to be obtained from some other source. Assume that this is supplied by potash feldspar which will also supply 0.28 mol Al_2O_3 and $6(0.28) = 1.68$ mols SiO_2 . The amounts of these last two substances, which were the only variables left, fall within the range specified by the formula. It is now possible to compute the batch weight.

Material	Formula	Mols	Mol. weight	Pounds	Per cent by weight
Zinc oxide.....	ZnO	0.1	81.4	8.1	2.4
Barium carbonate.....	BaCO_3	0.1	197	19.7	5.9
Borax.....	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.22	381	84.7	25.1
Tin oxide.....	SnO_2	0.3	151	45.3	13.4
Fluorspar.....	CaF_2	0.3	78	23.4	6.9
Feldspar.....	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	0.28	556	156	46.3
Total.....	337.2	100.0

There are, of course, many technological problems that are not taken up in this text in connection with the compounding of the above enamel. For example, it would be necessary to make a frit of all or of part of the

ingredients, including the borax because the latter is a soluble salt. Furthermore, it may be desirable to mix the ground frit with a little clay for ease of application. If this is done, adjustments in the batch will be necessary, such as decreasing the feldspar and supplying soda or potash from some other source. Technical problems of this sort are discussed in texts on ceramic technology; the above treatment serves to illustrate the method used to solve numerical problems.

PHASE DIAGRAMS

Chemical compounds that form when ceramic mixtures are heated can be predicted by reference to the phase diagram for the system under consideration. These diagrams show the composition of the minerals formed and the equilibrium relationships between solid and liquid phases. They are described in most books on general chemistry, and the various types of diagrams are discussed in more detail in texts on physical chemistry.¹ Phase diagrams of interest to ceramists have been compiled by Hall and Insley.²

It is sometimes necessary to know the relative quantities of liquid and of solid phases, or the percentages of the various crystalline phases, that are present in an equilibrium mixture. These quantities can be found by setting up equations for material balances containing them as unknowns, but the same information can be obtained more quickly by using certain geometrical relationships obtainable from the phase diagram. It is frequently possible to make an approximate estimate of the quantities desired by visual inspection alone. The method of doing this and the proof of the relationships are given below.

Two-component systems. Figure 11-1 shows a phase diagram for the system³ composed of substances *A* and *B*, which are completely

¹ For a thorough treatment of the phase rule and phase diagrams see J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Company, Inc., New York, 1951.

² F. P. Hall and H. Insley, *J. Am. Ceram. Soc.*, **16**, 463 (1933); Suppl., **21**, 113 (1938); *J. Am. Ceram. Soc.*, **30**, (11), pt. 2 (1947).

³ In the technical literature the term "system" has two meanings. In the first, the "system" is taken to mean that portion of the universe that one chooses to separate in thought from the rest of the universe (called the "surroundings") for purposes of considering physical and chemical changes in it as the conditions under which it exists are altered. Consideration is usually given to the energy interchange between the "system" and the "surroundings." In the second meaning the term "system" stands for all possible "systems" or aggregations of matter that can be derived from the particular chemical species under consideration. Thus, when one speaks of the "system CaO-SiO₂," he means to describe the equilibrium relations that exist for all possible mixtures from 100 per cent lime to 100 per cent silica and not be limited to a particular mixture of CaO and SiO₂.

It should be further understood that Fig. 11-1 is a section of a three-dimensional (*P-T-x*) diagram taken at a specific pressure.

miscible with each other in the liquid condition and which form no solid solutions or binary compounds. (In the ceramic field, MgO and CaO form a system of this type.) In the diagram, temperature is plotted against composition. The solid lines show the boundaries between phases; the dotted lines have been drawn for explanatory purposes.

Consider a mixture of A and B having the composition and temperature represented by the point X in Fig. 11-1. Let this mixture be cooled from X to Y to Z. At Y, solid A starts to crystallize. As A is deposited from

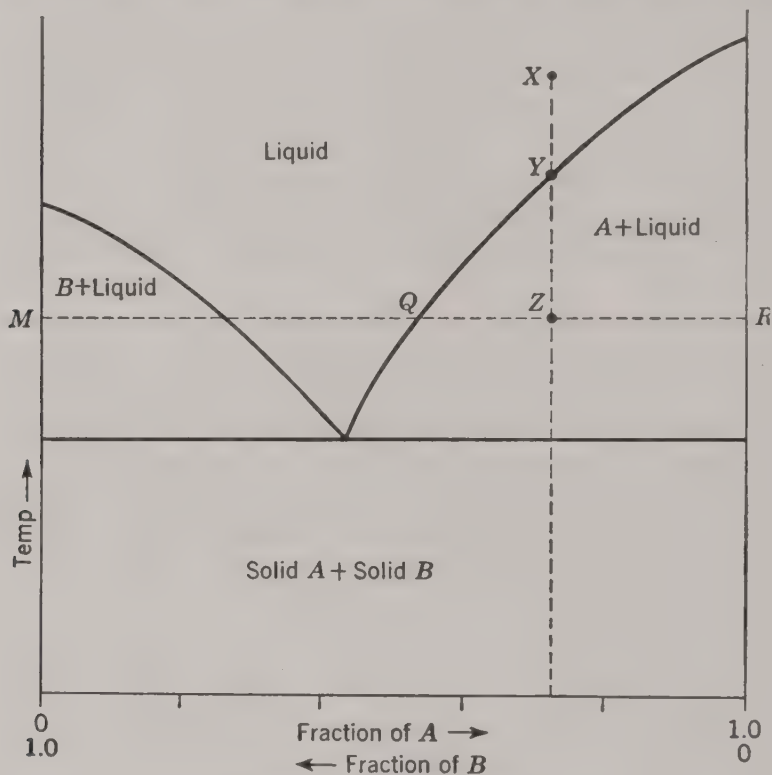


FIG. 11-1. System A-B.

solution, the latter becomes less rich in A and its composition changes along the curve YQ. Thus, at Z the system will consist of two phases; one is solid A, and the other is the remaining solution having the composition represented by the point Q. The question is, what are the relative quantities of these two phases?

Consider one unit (mol or pound) of the original solution. Let x = parts A which have solidified and $1 - x$ = parts of liquid remaining. Then the ratio $x/(1 - x)$ is the quantity sought.

An equation containing x may be written by setting up a material balance as

$$(A \text{ in solid}) + (A \text{ in remaining solution}) = (A \text{ in original solution})$$

To complete the writing of the equation it is necessary to know the composition of each phase in addition to its quantity. The solid, of course, consists entirely of A . The fraction of A in the remaining solution is MQ , the length of this line being read on the scale at the base of the diagram. Similarly, the fraction of A in the original solution is MZ . To be consistent and use line lengths throughout to express compositions, the composition of A is MR , which is the unit width of the diagram. The material balance then becomes

$$(x)MR + (1 - x)MQ = (1)MZ$$

This gives

$$x = \frac{MZ - MQ}{MR - MQ} = \frac{QZ}{QR}$$

and

$$(1 - x) = 1 - \frac{QZ}{QR} = \frac{QR - QZ}{QR} = \frac{ZR}{QR}$$

Dividing the first expression by the second gives

$$\frac{x}{1 - x} = \left(\frac{QZ}{QR}\right)\left(\frac{QR}{ZR}\right) = \frac{QZ}{ZR}$$

Thus, the ratio of solid A to remaining solution, or $x/(1 - x)$, is the ratio of the length of the line QZ to the length of the line ZR . These can be scaled off and actual numbers substituted for the line lengths to obtain a numerical result. If the scale is in weight fractions, the result is a weight ratio; if it is in mol fractions, the result is a molar ratio. An important precaution to observe in using molal units is pointed out below.

The conclusion reached above may be stated as the following rule: *When a mixture separates into two phases whose compositions are indicated by points at the ends of a straight line passing through the original composition point, then this point divides the line into segments that are inversely to each other as the quantities of the two phases.* In this statement the term "inversely" refers to the fact that the segment that includes the point of composition of one phase refers to the amount of the other phase. In the proof given, the segment QZ includes the composition point Q for the *liquid*, but the length of this segment refers to the quantity of *solid*. This rule is commonly referred to in the literature as the "lever rule" from the similarity between it and the rule of mechanics governing the inverse proportionality between forces and the arms of a lever to which they are applied.

Figure 11-2 is for the system A - B when the single binary compound AB is formed. It will be noted that the vertical line drawn through the composition AB divides the diagram into two parts, each like Fig. 11-1.

To illustrate an important difference between diagrams using mol per cent and those using weight per cent it will be assumed that the molecular weight of *A* happens to be equal to the molecular weight of *B*; thus, the weight-per cent diagram and the mol-per cent diagram appear identical.

Assume that a mixture of 20% of *A* and 80% of *B* is heated slowly until melting begins and that it is held at this temperature (while continuing to add heat) until further addition of heat would cause a rise in temperature. How much of the original mixture is liquefied?

The mixture is represented by the point *P* and is at the temperature T_1 . The liquid phase contains 30% of *A* and the unliquefied solid is

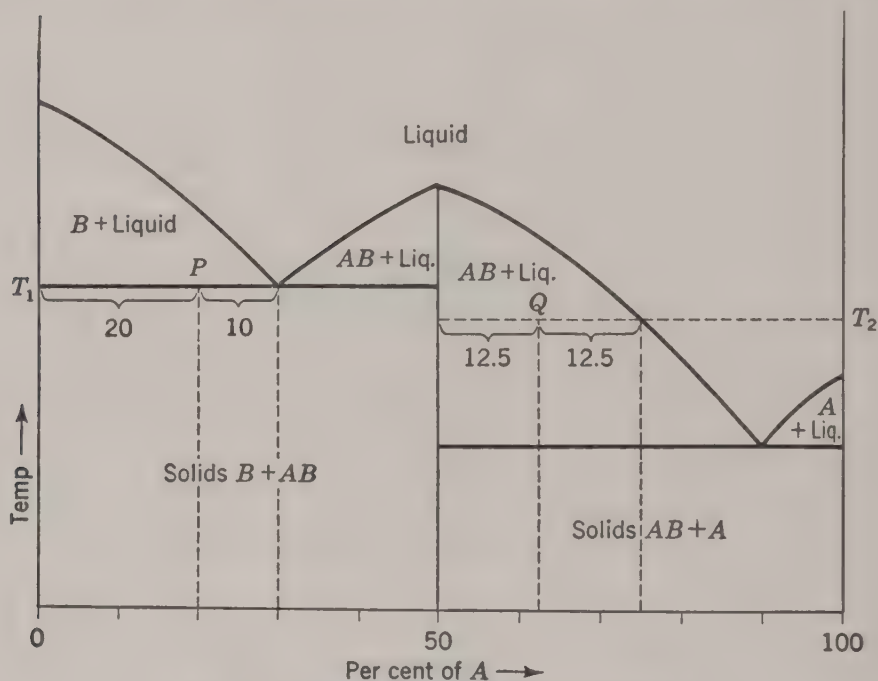


FIG. 11-2. System A-B with binary compound.

pure *B*; *i.e.*, all the *A* has gone into solution with some of the *B*. From the lengths of the segments of the horizontal line passing through *P* and joining the compositions of the solid and liquid phases, it is seen that the ratio of liquid to solid is 20:10; *i.e.*, two thirds of the original mixture has liquefied, and one-third remains as solid.

Assume that a second mixture containing 62.5% *A* and 37.5% *B* is heated to T_2 and is held there until equilibrium is established. What is the condition of the system?

This temperature and composition are located on the diagram at the point *Q*, in the field marked "*AB* + liquid." The ratio of solid *AB* to liquid is 12.5:12.5; in other words, the system is composed of 50% liquid and 50% solid.

Now assume that this problem is to be solved in terms of molar units.

Since the molecular weights of A and B are equal, the same diagram is used. The point Q representing the temperature and composition of the system is also at the same point in the diagram.¹ At first glance it would appear that there are 12.5 mols of solid to 12.5 mols of liquid, but as the molecular weight of AB is twice that of either A or B , this would mean twice as much solid by weight as liquid. Since this is a different result from what was obtained before, it is impossible. The difficulty is caused by the fact that the scale of compositions reads in per cent of A (or B) and not in per cent of the compound AB . With this in mind, it is correct to say that 12.5 mols of A plus B (*i.e.*, 6.25 mols of each) have combined to form 6.25 mols of AB , and 12.5 mols of A plus B are left as liquid. Thus, when a compound is formed it must be remembered that the line segment referring to it gives the proportionate quantity of the total mols of A and B in the compound. The mols of the latter can be found by dividing by n , where n is the total number of mols of A and of B needed to form 1 mol of the compound. As an example, the compound $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is composed of 8 total mols of CaO and Al_2O_3 . In this case there are one-eighth as many mols of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ as there are mols of the individual oxides used in forming the compound.

Most diagrams have compositions expressed in weight units for reasons of practicality. Reference to the literature, however, shows that many diagrams are on a molar basis, especially when more than one system is shown on the same plot, so this precaution needs to be observed to avoid erroneous results.

Three-component systems. A three-component system is generally represented by means of a triangular diagram. This is an artifice to enable three compositions to be plotted on a plane surface, which has, of course, only two independent dimensions. An equilateral triangle² as in Fig. 11-3 is used, and its side is made equal to unity or to 100. Each vertex represents pure A , B , or C ; a point D along one side is a mixture of two components; and a point E in the interior represents a mixture of all three components.

The composition of a three-component mixture is found by getting the perpendicular distances from the point of composition to each side of the triangle. It is a property of equilateral triangles that the sum of these three perpendicular distances is constant (and in this case made 100%) wherever the point may be located. For convenience, these distances are usually read on the scales that are placed along each side of the triangle. In the figure, E is a mixture of 35% A , 55% B , and 10% C .

¹ When the molecular weights of A and B are different, as they generally are, the shift of a point to right or left when going from the weight diagram to the molar diagram automatically takes this difference into account.

² Only diagrams based on equilateral triangles are considered in this text, but right triangles and even scalene triangles may be used to represent three-component systems.

Since the two dimensions of a plane surface are used to represent composition, the dimension of temperature is represented by distances perpendicular to the plane of the triangle. The liquid-solid boundaries appear as curved *surfaces* in the prism thus formed, whereas they appeared as *lines* in the T, x diagram for a two-component system. Thus complete representation of a three-component system would require a solid, prismatic model.

However, if planes be passed through this model at various temperature levels they will intersect the solid-liquid surface in lines that can be projected onto the triangular diagram of compositions as a series of

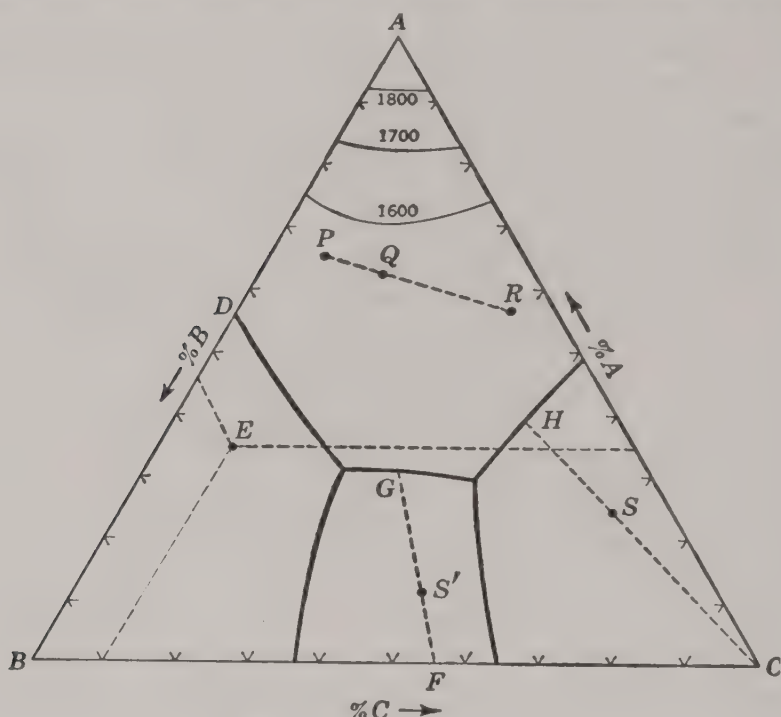


FIG. 11-3. System A-B-C.

contour lines. Three such lines for 1800, 1700, and 1600° are shown in the field where A is in equilibrium with the solution. This is the way that the temperature-composition relationships of a three-component system are generally shown. In fact, these planar diagrams are somewhat more convenient to use than an opaque, solid model on which linear distances would be difficult to scale.

For the various types of three-component systems, reference should be made to texts on physical chemistry dealing with this particular subject. The reader should also consult Hall and Insley's compilation of diagrams of ceramic systems. It will be sufficient to show in Fig. 11-3 certain relationships that are useful in the solution of problems.

1. If mixture P is added to mixture R, the combined mixture Q lies

on a line joining P and R and the distances QR and PQ are in the ratio of the amounts of P and R mixed. Likewise, if Q is separated into P and R , the ratio of the amount of P to R is given by the ratio QR/PQ . This statement and its corollary are simply extensions of the similar principle developed for two-component systems.

2. If solution S separates pure C , then the composition of the remaining solution must change along the line SH , which is an extension of the line drawn through C and S . A little consideration will show that the line HSC is the locus of all points having the same ratio of A to B as did the original solution S and that this is a necessary criterion for solutions to which pure C is added, or from which it is removed.

3. If solution S' separates material having the composition F , then the solution changes in composition in the direction of $S'G$. Conversely, if a solution S' is changing at some particular moment in the direction indicated by $S'G$, then the solution is separating, at that moment, material having the average composition of F (assuming that no ternary compounds are separated).

Figure 11-4 shows the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. Application of prin-

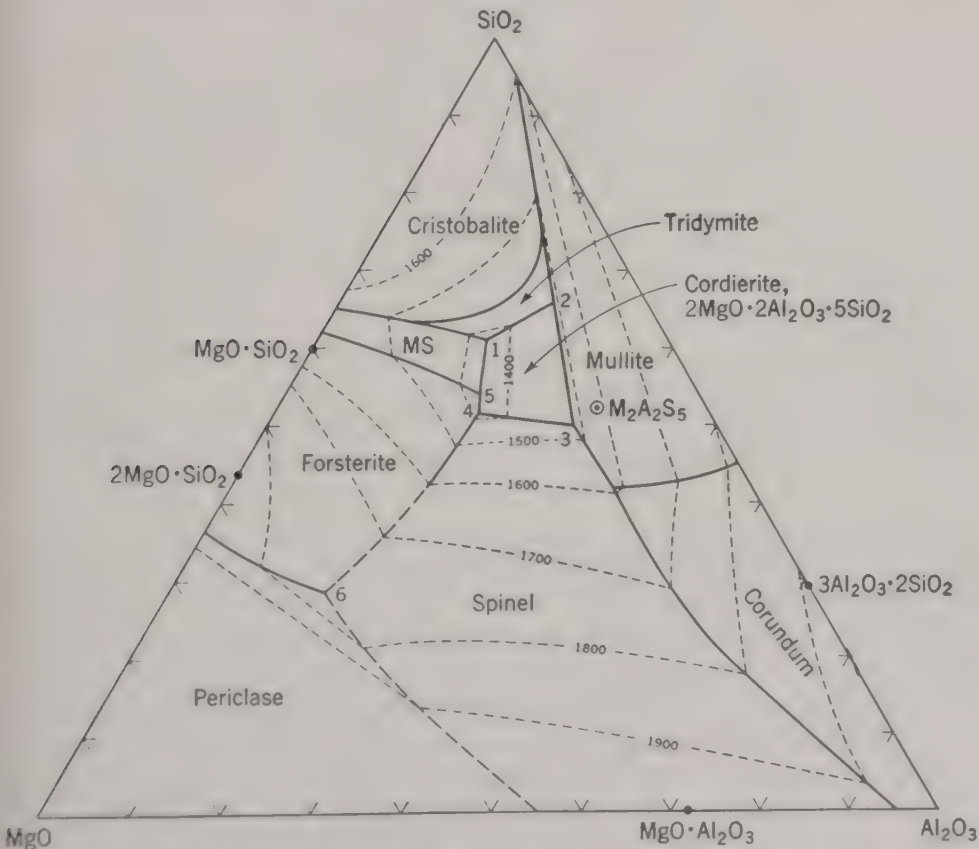


FIG. 11-4. System $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. [Rankin and Mervin, *Am. J. Sci.* 45, 301 (1918).]

ciples developed in the preceding paragraphs will be illustrated by a problem dealing with this system.

Illustration 4. A mixture containing 33.3% each of MgO , Al_2O_3 , and SiO_2 is heated until it is completely fused. Describe the path of crystallization and tell what substances are crystallized during each step of the path and in what amounts they are produced.

Solution. The solution to this problem is indicated in the skeleton diagram for this system as shown in Fig. 11-5. The original mixture is

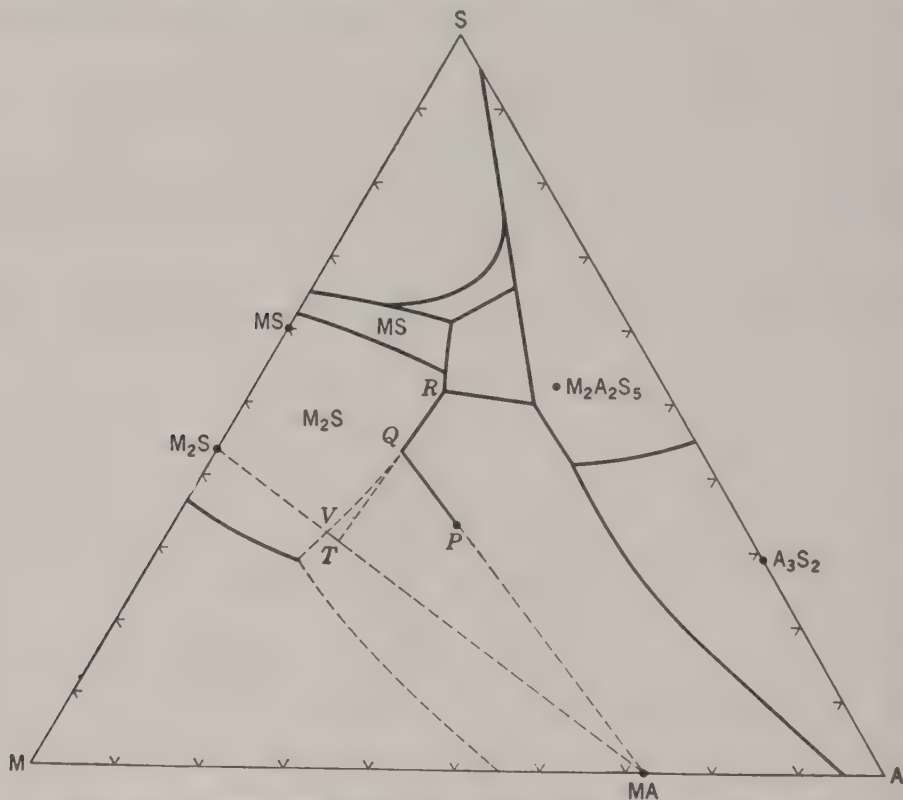


FIG. 11-5. System $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (used for solution of Illustration 4).

designated by the point P . Since spinel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, is the first substance to crystallize, the path of crystallization (by which is meant the line showing the composition of the solution) follows PQ , which is obtained by drawing a line through MA and P . At Q , forsterite, $2\text{MgO} \cdot \text{SiO}_2$, appears and crystallizes simultaneously with spinel. The path of crystallization then follows the boundary between the two fields, namely, QR . Since a mixture of forsterite and spinel is separating and since all possible mixtures of these two substances must fall on the line joining M_2S and MA , the average composition of the mixture that separates at Q is given by the point T on this line. This point is located by taking the direction of the path of crystallization from Q on (*i.e.*, by taking the

tangent to the curve QR at the point Q) and projecting back to the line M_2S - MA . It so happens that, in this problem, QR is practically a straight line; thus, the average composition separating throughout the path QR remains substantially constant. If QR had been curved, the average composition at the start and at the end of the path would be taken and a mean value of these averages would be used.¹

At R , which is an invariant or quadruple² point, cordierite, $M_2A_2S_5$, appears and there are now four phases—spinel, forsterite, cordierite, and liquid. The system remains at R , which means that neither the temperature of the system nor the composition of any phase can change until one of the phases disappears; in this case it will be the liquid.

Crystallization along path PQ . The ratio of the length of the segments PQ and P - MA can be obtained by laying a scale on the diagram or by using any other pair of proportionate lengths such as the percentages of Al_2O_3 as read along the base of the triangle. If the latter, they are $33.3 - 21.5 = 11.8$, and $71.7 - 33.3 = 38.4$, respectively. Thus, the solid spinel that has separated by the time Q is reached is to the solution remaining as 11.8 is to 38.4, or the solid is

$$100(11.8)/(11.8 + 38.4) = 23.5\%$$

of the original solution. The solution remaining is 76.5% of the original, and its composition is 35.5% MgO , 21.5% Al_2O_3 , and 43% SiO_2 .

Crystallization along path QR . The average composition of the material crystallized along this path has the composition represented by T , which, from the respective lengths of M_2S - T and T - MA , is 20 parts of spinel to 51.7 parts of forsterite. QR is to QT as $(35.5 - 26)$ is to $(45 - 35.5)$, these values being read by projection to the MgO scale. That is, the solid mix of forsterite and spinel produced along path QR is equal to the quantity of solution remaining. There being 76.5 parts of solution at the start of this path, 38.2 parts have crystallized, leaving 38.3 parts of solution at R . The composition of the latter is 26% MgO , 23% Al_2O_3 , and 51% SiO_2 . In terms of the individual minerals crystallizing, the quantities per 100 parts of original solution are

$$\begin{aligned} 38.2(20/71.7) &= 10.6 \text{ parts spinel} \\ 38.2(51.7/71.7) &= 27.6 \text{ parts forsterite} \end{aligned}$$

Crystallization at point R . The amount of each substance crystallizing from the 38.3 parts of solution remaining at this point is found by using unknowns and writing material balances.

¹ Except for certain cases where one of the phases may disappear.

² See texts on physical chemistry for a discussion of the phase rule for a definition of this and other technical terms that are used to describe equilibria between phases. Some authors call R a quintuple point, counting the gas phase and making five phases in all. But if the pressure is specified as 1 atm, there will be no gas phase.

Let x = amount of spinel (composition, 28.3% MgO, 71.7% Al_2O_3)
 y = amount of forsterite (composition, 57.4% MgO, 42.6% SiO_2)
 z = amount of cordierite (composition, 13.8% MgO, 34.9% Al_2O_3 ,
 51.3% SiO_2)

$$\text{MgO balance: } 0.283x + 0.574y + 0.138z = 0.26(38.3)$$

$$\text{Al}_2\text{O}_3 \text{ balance: } 0.717x + 0.349z = 0.23(38.3)$$

$$\text{SiO}_2 \text{ balance: } 0.426y + 0.513z = 0.51(38.3)$$

The equation $x + y + z = 38.3$, which is a total material balance, can be used, but it is not an independent equation.

Solving these equations gives

$$x = -1.7 \text{ parts spinel}$$

$$y = 11.3 \text{ parts forsterite}$$

$$z = 28.7 \text{ parts cordierite}$$

The significance of the negative result for spinel is that a small amount of this material redissolves. This must be so in order that the oxides may be in the proper proportions to form the minerals without having any of the individual oxides left over, a result that would be impossible since the individual oxides cannot exist at this point.

It may be emphasized here that this solution to the problem is for *equilibrium* conditions. If some of the spinel did not dissolve, or if the solution were cooled too rapidly, its composition might coast along the line from 4 to 5 to 1 in Fig. 11-4 and produce a small amount of phases other than those mentioned. Since equilibrium between the last portion of liquid to crystallize and the large mass of crystals already formed is difficult to obtain, something of this nature might be expected if this problem were to be carried out experimentally.

Recapitulation. As a check on the numerical results it will be well to compute the quantity of individual oxides in the minerals formed and see if the total agrees with the starting mixture.

	MgO	Al_2O_3	SiO_2
Spinel:			
(23.5 + 10.6 - 1.7)0.283.....	9.2		
(23.5 + 10.6 - 1.7)0.717.....	23.2	
Forsterite:			
(27.6 + 11.3)0.574.....	22.3		
(27.6 + 11.3)0.426.....	16.6
Cordierite:			
(28.7)0.138.....	3.9		
(28.7)0.349.....	10.0	
(28.7)0.513.....	14.7
Total.....	35.4	33.2	31.3

MgO is 2 per cent too high and SiO₂ is 2 per cent too low, these discrepancies being produced by slight inaccuracies in reading the diagram.

Improving refractory compositions. The temperature lines of Fig. 11-4 show that a mixture of one-third each of magnesia, alumina, and silica does not make a good refractory material. This mixture is 76.5% liquid at *Q* (Fig. 11-5) where the temperature of the system is 1600°C (P.C.E.¹ of 26). On further cooling, crystallization is completed at *R* at a temperature of 1370°C (cone 13 to 14). This is the temperature at which fusion starts when this mixture is heated. Correspondingly low temperatures will apply to any mixture on the side of the line joining M₂S and MA that is toward S. Mixtures whose compositions lie on this line will complete crystallization (or will commence to fuse if heated) at the temperature corresponding to the point *V* where this line intersects the forsterite field. This is about 1740°C (cone 33). Mixtures lying on the MgO side of this line will complete crystallization at point 6 in Fig. 11-4, which is 1700° (cone 32). These temperatures are for mixtures made from pure substances; for commercial materials containing impurities, the temperatures are lower.

From this discussion it should be obvious that compositions of interest as refractory materials must lie on the MgO side of the line joining M₂S and MA. It should be equally clear that compositions lying on the other side of the line can be "corrected," *i.e.*, improved in refractoriness, by adding enough magnesia to bring the composition to the line or beyond it. In actual practice a considerable excess is used to ensure complete conversion, especially since the unreacted magnesia will do no harm. This is the basis of several patents.² The following illustration shows how this idea may be applied.

Illustration 5. Norton³ gives this analysis of chromite from New Caledonia:

	<i>Per cent</i>
Cr ₂ O ₃	54.5
SiO ₂	3.1
Al ₂ O ₃	11.0
FeO.....	19.5
CaO.....	1.5
MgO.....	8.0
Total.....	97.6

What is the minimum quantity of MgO that should be added to 100 lb of this ore to give it maximum refractory quality?

¹ Pyrometric Cone Equivalent.

² G. E. Seil, U.S. Patents 2028018 and 2060697.

³ F. H. Norton, "Refractories," 3d ed., p. 54, McGraw-Hill Book Company, Inc., New York, 1949.

Solution. Chromite when pure has the formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. This mineral is a spinel, and part of the FeO can be replaced by MgO and part of the Cr_2O_3 by Al_2O_3 . The interchangeability of Cr_2O_3 and Al_2O_3 is further indicated by the phase diagram for these two substances, which shows a complete range of solid solutions between them. Increasing MgO and Cr_2O_3 will raise the fusion point of the spinel; on the other hand, increasing FeO and Al_2O_3 will lower it. Thus, except for CaO , which may be neglected in these calculations, chromite ore may be considered as a three-component system: $\text{RO} \cdot \text{R}_2\text{O}_3 \cdot \text{SiO}_2$, where $\text{RO} = \text{MgO}$ or FeO , and $\text{R}_2\text{O}_3 = \text{Cr}_2\text{O}_3$ or Al_2O_3 .* In the diagram for this system there will be a spinel field. Also there will be a field for $(\text{Mg}, \text{Fe})_2\text{SiO}_4$, since fayalite, Fe_2SiO_4 , and forsterite, Mg_2SiO_4 , form a complete series of solid solutions known as the olivines. The fields for spinel and olivine may be expected to have a common boundary, as they did in Fig. 11-5.

The solution of this problem may now be simplified by converting the analysis of the ore to a molal basis.

Basis: 100 lb ore.

	Pounds	Mol. weight	Mols RO	Mols R_2O_3	Mols SiO_2
Cr_2O_3	54.5	152	0.358	0.052
SiO_2	3.1	60	
Al_2O_3	11.0	102	0.108	
FeO	19.5	72	0.271		
MgO	8.0	40.3	0.198		
Total.....	0.469	0.466	0.052

Mols MgO needed for $2\text{MgO} \cdot \text{SiO}_2 = 2(0.052)$ 0.104

Excess MgO present, $0.469 - 0.466$ 0.003

Minimum MgO to be added 0.101

Pounds MgO , $0.101(40.3) = 4.1$

As was pointed out previously, a considerable excess would be used, the amount being determined by experiment.

PROBLEMS

1. The following table gives the chemical compositions of six commercial feldspars.

* Note that in this problem the symbols RO and R_2O_3 are used in a somewhat different sense from that in which they were used in the earlier part of this chapter. Here, R^{II} in RO and R^{III} in R_2O_3 stand for atomic replacements in the actual crystal structure where isomorphism is possible. In fact, it may not be necessary to neglect calcium, since forsterite at least exhibits a limited tolerance for replacement of magnesium by calcium.

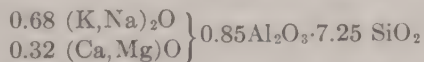
No.	SiO ₂ , %	Al ₂ O ₃ , %	CaO, %	Na ₂ O, %	K ₂ O, %	Fe ₂ O ₃ , %	MgO, %	Ignition loss, % (includes H ₂ O)
1	65.1	19.5	0.3	2.59	12.26	0.20	0.02	0.32
2	65.2	19.7	0.3	1.25	12.19	0.15	trace	1.18
3	68.7	17.9	0.5	3.43	9.15	0.16	trace	0.34
4	70.9	17.5	0.3	3.89	6.41	0.12	trace	0.84
5	73.1	15.4	0.8	5.57	4.52	0.06	trace	0.56
6	67.4	20.0	0.5	10.03	1.04	0.27	0.02	0.50

Recalculate these analyses in terms of molecular composition. Find the formula weight for each spar.

2. A feldspar subjected to chemical analysis yields the following results: SiO₂, 69.92%; R₂O₃, 17.72%; CaO, 2.98%; MgO, 1.91%; loss on ignition, 0.62%. The alkalis were not determined. Assuming first that the undetermined constituent consists only of K₂O and, second, that it is one-half K₂O and one-half Na₂O, what is the empirical molecular formula for this feldspar?

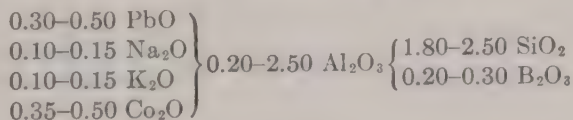
3. The average composition of bone china is 34% kaolin, or china clay, 17% feldspar, 12% flint, and 37% bone ash. Recalculate this composition in terms of the molecular composition of the fired ware.

4. Cone 14 porcelain glaze has the following average composition:



A batch of this material has been made up using feldspar No. 3 of Prob. 1. What substances and how much would be used to complete the batch?

5. An excess of the raw glaze of Prob. 4 is available and it is desired to modify some of it to make an earthenware glaze for glost firing at cones 2 to 4. The finished glaze is to have a composition within the following formula:



Is it possible to do this? If so, per 100 lb of the porcelain glaze what other materials must be used and in what amounts?

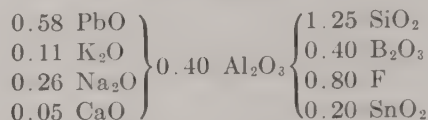
6. The batch weight for an enamel for sanitary ware is as follows: feldspar, 120; borax, 125; soda ash, 16; niter, 10; fluorspar, 40; red lead, 80; zinc oxide, 30; tin oxide (SnO₂), 50. This is fritted, ground, and then dusted on the ware. What is the empirical formula for the composition of the enamel?

7. The following batch is fritted: spar, 126 parts; white sand, 76 parts; borax, 98 parts; red lead, 15 parts; soda ash, 16 parts; niter, 14 parts; fluorspar, 14 parts; cryolite, 44 parts. Then 100 parts of frit are mixed with 7 of clay and 0.5 of magnesium carbonate and made into a slip with 40% of water. What is the molecular composition of the enamel?

8. The following batch makes 1000 lb of frit for a steel ground coat: borax, 365; feldspar, 400; flint, 256; soda ash, 115; sodium nitrate, 51; fluorspar, 77; cobalt oxide (Co₃O₄), 4½; manganese dioxide, 12¼. Each 100 lb of frit is milled with 6 lb of clay

and 2 lb of borax. The feldspar used contains 66.82% SiO_2 , 18.96% Al_2O_3 , 9.20% K_2O , 3.65% Na_2O . What is the composition of the final enamel?

9. How would you make up an enamel to have the following composition?



10. The following diagram for the system Al_2O_3 - SiO_2 * has added to it the deformation temperatures, obtained by the U.S. Bureau of Standards¹ for those Orton standard pyrometric cones that consist of mixtures of alumina and silica. The deformation

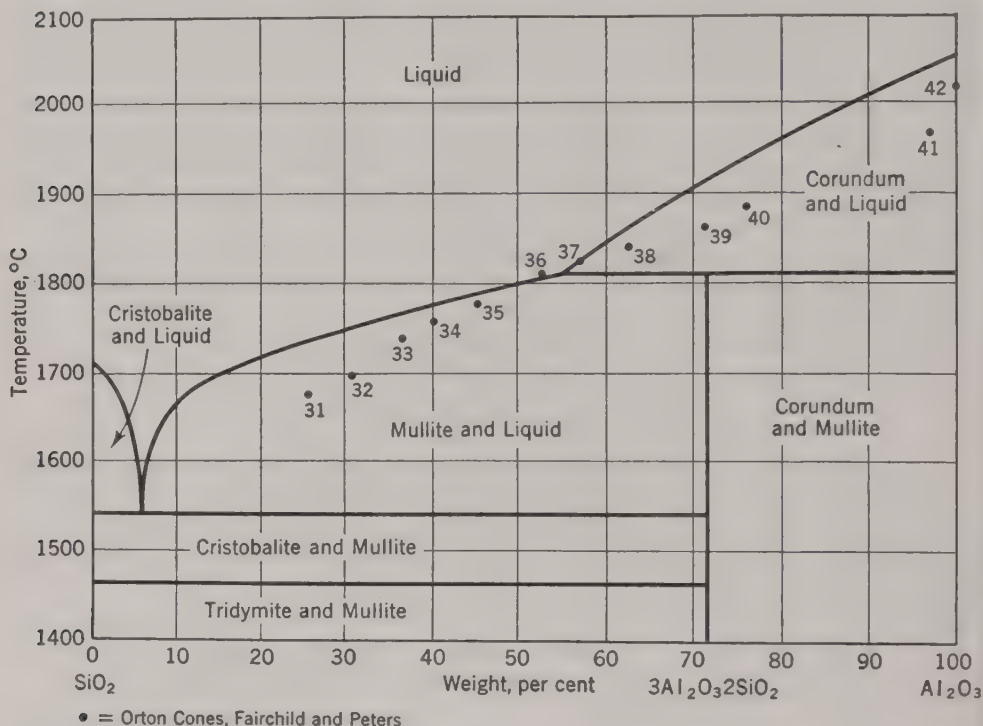


FIG. 11-6

temperature is the "end point," or the temperature when the cone is "down." What is the percentage of liquefaction of cone 31 when it is down? Of cones 32, 33, 34, respectively, when they are down? Assume that equilibrium conditions are reached in the heating process.

11. If cone 31 is heated until cone 32 is down, what percentage of the former is now liquid? If heated to cone 33?

12. The bending interval for cone 31 is 25°C . What is the condition of this cone when it starts to bend? When it is down?

13. Cone 35 is supposed to be pure Florida kaolin. How do you explain the position of this point on the diagram?

* N. L. Bowen and J. W. Greig, *J. Am. Ceram. Soc.*, 7, 242 (1924).

¹ C. O. Fairchild and M. F. Peters, *J. Am. Ceram. Soc.*, 9, 700 (1926).

14. A large part of the white ware manufactured in the United States is made from the three components clay, flint, and feldspar, with occasional secondary fluxes, such as lime and magnesia, in small amounts. All possible combinations of the three principal components can be shown on the following triaxial diagram in which the three vertices represent 100% pure components. While it might be more logical in a diagram of this kind for the clay vertex to represent $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, the usual practice is to include the water of composition. Commercial feldspars usually contain an excess of Al_2O_3 and SiO_2 over that represented by the formula, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, and the excess may

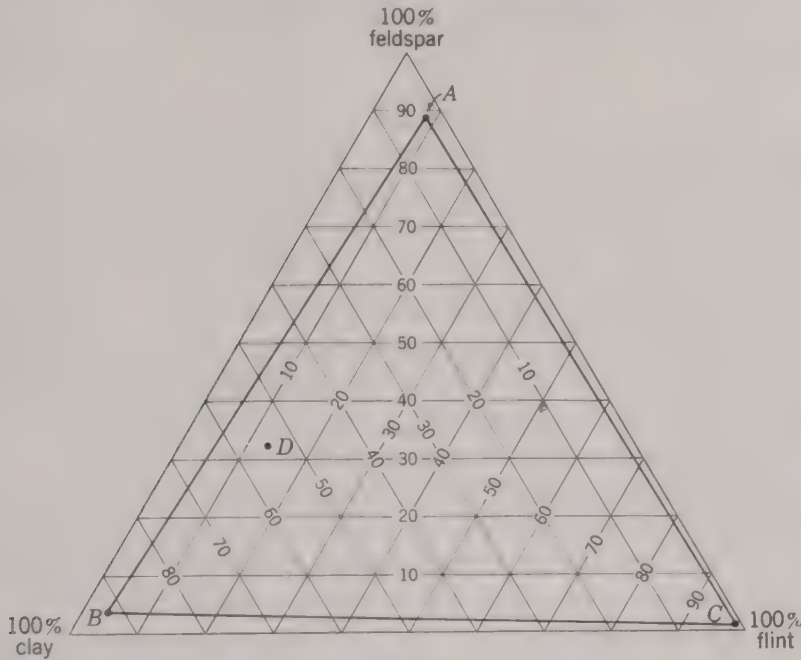


FIG. 11-7

be calculated as the equivalent of so much clay substance and flint in addition to pure feldspar. Thus a commercial feldspar may be represented by the point *A* on the diagram. Similarly, point *B* represents a typical clay and point *C* a commercial grade of flint or ground quartz. All mixtures of *A*, *B*, and *C*, such as *D*, are within the triangle joining the first three points. Show from the geometry of the diagram how to find the proportions of *A*, *B*, and *C* used to make up *D*.

15. Prove that your solution to Prob. 14 is correct by recalculating the composition of a feldspar, clay, and flint known to you in terms of the pure substances. Then take a mixture of 50% of this feldspar, 30% of this clay, and 20% of flint, locate its composition on the diagram, and show that you would arrive at the same point if you used the geometric method.

Chapter 12

DESIGN PROBLEMS

Industrial stoichiometry serves two main purposes. The first of these is the analysis of data representative of existing plant operations by the calculation of quantities otherwise difficult of direct measurement, thus providing information which, without the aid of this tool, would be entirely wanting or at best only empirical and qualitative. Calculations of this kind are quite often the simplest and cheapest way of obtaining an accurate and quantitative vision of what is actually taking place within a process. In preceding chapters, discussion has been devoted primarily to illustrations of this important function.

The second and no less important purpose is the use of laboratory data as a basis for estimating large scale production. One type of problem falling under this head is the design of equipment for a process from the data on the physical and chemical characteristics of the materials involved. Another type is the design of large-scale units from data obtained by laboratory experimentation upon a process in the development stage. These two types of problems are discussed in this chapter.

As an example of the first type, the tunnel kiln is widely used for burning brick and other ceramic ware. The detailed design of a kiln and furnace involves the chemistry of combustion, flow of fluids, transmission of heat by radiation and conduction, the complicated chemical relationships of the particular reactions for which the furnace is built, the choice of suitable refractories, proper mechanical construction, provision for insulation, ease and accuracy of operating control, laborsaving devices, and many other related factors, which are beyond the scope of this book. However, the first step that must be taken is the solution of the stoichiometric problems involved, particularly the material and heat balances.

In every problem of design, certain conditions are fixed by the very nature of the case. These are generally the throughput desired, the minimum or maximum temperatures that must be reached within a process, the temperature and quantity of cooling water available, and the like. On the other hand, the designing engineer himself will make

certain assumptions. These assumptions are frequently equivalent to setting up an ideal, which may or may not be possible of actual realization. The designer must base his computations on both fixed conditions and assumptions and must check his conclusions with the greatest care to make sure that the final design is a consistent one.

In the solution of complicated problems of this sort, one or more of the assumptions are almost always found to be incompatible with the others. In such cases the assumptions must be revised and the design modified accordingly. The methods of stoichiometry are invaluable for the elimination of errors by cross checking of this sort.

To a greater or less degree, such computations involve methods of trial and successive approximations. General rules of procedure are difficult to give. It will probably be most helpful to discuss a specific case.

DESIGN OF A TUNNEL KILN

Assume that it be required to design a gas-fired tunnel kiln, operated continuously, for the burning of a ceramic material which passes through the tunnel in a direction countercurrent to that of the gases. The stock enters at one end of the tunnel and in progressing toward the middle is preheated by the sensible heat of the hot products of combustion flowing in the opposite direction. This section of the tunnel will be called the preheating zone. Combustion takes place at the middle of the tunnel (combustion zone), where the stock is heated to the maximum temperature of burning. The stock now passes through the remaining section of the tunnel (cooling zone), in which it is cooled partly by means of the air necessary for combustion and partly by loss of heat through the walls.

Consider the flow of gases. Air enters the end of the tunnel at which the stock leaves. The air is preheated by the cooling stock, thereby conserving heat in the operation of the kiln. The preheated air combines with the fuel, which is admitted to the combustion zone, and the hot products of combustion flow countercurrent to the movement of the stock in the preheating zone, going to the stack at the end of the kiln where the stock enters.

The stock has been carefully dried before it comes to the kiln. It is placed on cars, one of which is pushed into the kiln every 4 hr, pushing out a similar car at the other end. The firing of the furnace is continuous. The number of cars in the kiln is so large that no serious error will be made in assuming that the movement of the stock is also continuous. The lower part of each car is constructed of steel and cast iron, weighing 1000 lb; the upper part consists of refractory, weighing 2000 lb; and the charge weighs 6000 lb. The specific heat of the refractory may be taken as $0.20 + 0.0001t$ and that of the charge as $0.22 + 0.00012t$, t

being in degrees centigrade. In the range from 600 to 700°C, the charge loses its combined water, of which it contains 6.2%. The heat of decomposition of the clay with evolution of combined water, expressed per gram mol of water lost, is estimated to be 15 kcal. After this decomposition, the specific heat of the charge may be taken as that of the refractory given above. Stock, air, and gas enter the kiln at 20°C. The stock must be burnt to 1210°C, and the temperature rise and fall as it passes through the kiln must be substantially uniform.

The burning schedule demanded by the characteristics of the stock involves 200 hr in the kiln. Since the cars are 6 ft long, this requires a kiln length of 300 ft, of which 150 ft must be in the preheating zone, 15 ft in the combustion zone, and 135 ft in the cooling zone.

The preceding may be taken as the fixed conditions which, in any case, the kiln must be designed to meet. These are not subject to alteration. On the other hand, it is very desirable to cool the stock to 160°C before it leaves the kiln and to preheat it before it enters the combustion zone to 1110°C. Furthermore, while such a kiln will be carefully insulated against loss of heat, its surface area is so large that the heat lost by conduction and radiation through the walls is sure to be considerable. The insulation will be more or less proportioned to the temperature of the kiln at the point in question, so that, as an approximation, the heat loss per unit length may be taken as constant. For the conditions under which this kiln is to operate, it is claimed that it will not pay to insulate beyond reducing the heat loss per foot of length to 9000 Btu per hour in the preheating and combustion zones and to 80% of this in the cooling zone. The loss in the latter is less because the gases and hence also the kiln walls are cooler than the stock, rather than hotter as in the rest of the kiln. It will probably be inadvisable to cool the stack gases below 240°C, or to preheat the air above 1000°C. The metal of the cars and the lower part of the refractory base are protected from the full heat of the kiln. Failure of the refractory to come up to temperature is more or less counterbalanced by heat picked up by the metal. Consider this counterbalancing exact, *i.e.*, assume all the refractory brought to full temperature but the metal not heated at all. The foregoing figures represent tentative assumptions on which to attempt a design.

It is required to design such a kiln, using as fuel a natural gas, which may be assumed substantially CH_4 . It is further desired to modify the design so that the furnace can replace this fuel with producer gas of the following composition: 7% CO_2 , 21% CO , 15% H_2 , 1% CH_4 , and 56% N_2 . Finally, the fuel saving which can be realized by an increase in insulation sufficient to halve the heat loss by conduction and radiation is to be estimated.

Solution. This kiln consists of three separate sections, namely, the preheating, combustion, and cooling zones. If heat balances can be set up for each of these zones, information which is absolutely dependable will be obtained regarding the operation of the kiln. The relationships existing in the cooling zone are less complicated than those in the other two. It is, therefore, advisable to set up a heat balance for this zone first.

The heat supply to this part of the kiln comes solely from the sensible heat of the burnt stock, which enters this zone at 1210°C and cools to 160°C . The average temperature of the stock in this zone is, therefore, $(1210 + 160)/2 = 685^{\circ}\text{C}$. At this temperature the specific heat of the stock, from the formula $0.20 + 0.0001t$, is 0.2685, which is the average specific heat between the temperature limits quoted because the specific heat is linear with the temperature. The heat given up by the stock is, therefore, its weight times its temperature drop times this specific heat. In burning, the 6000 lb of stock on each car loses 6.2 per cent of water, leaving a burnt-stock weight of 5630 lb. Adding the weight of the refractory base of the car gives a car weight of 7630 lb. Therefore, on an hourly basis, the heat supplied to this zone is

$$(7630/4)(1210 - 160)(1.8)(0.2685) = 967,000 \text{ Btu/hr}$$

The radiation loss is $9000(0.8)(135) = 972,000 \text{ Btu/hr}$. This shows the heat loss by radiation to be greater than the heat supplied to the cooling zone, absolutely no heat being available for preheating the air. There is obviously something wrong with the assumptions. The difficulty lies in the fact that the assumed radiation loss is excessive. If a kiln were to be constructed to have this radiation loss, the stock would be cooled by radiation alone in less than 135 ft. Since the firing schedule demands that the stock be not cooled more quickly than this, it of necessity follows that the radiation loss must be reduced, at least in the cooling zone.

The difference between the radiation loss and the sensible heat in the stock is so small that the kiln could be built and operated by the use of a very slightly increased amount of insulation, provided no air whatever be drawn through the cooling zone but only cold air be supplied at the burners. However, it scarcely seems wise to construct the kiln in this way. It is, therefore, better to design for a smaller radiation loss, increasing the insulation if necessary to accomplish this result, so that the air passing through the cooling zone will pick up and usefully recover some heat. In order to get information on the extent to which it is advisable to insulate, the problem will be solved (1) for a heat loss in the preheating and combustion zones of 8000, and (2) for a heat loss of 4000 Btu/hr per

foot of length. The loss in the cooling zone will, as before, be 80% of that in the other two zones.

Repeating the computation made above for a heat loss of 80% of 8000 Btu/hr per foot of length in the cooling zone, the heat lost through the walls is 864,000 Btu/hr and the heat usefully picked up by the incoming air is $967,000 - 864,000 = 103,000$ Btu/hr.

When an attempt is made to set up a heat balance on either the combustion zone or the preheating zone, it will soon develop that there are three unknown quantities: the amount of gas used by the kiln, the amount of excess air employed, and the temperature at which the gases leave the combustion zone. Only two heat balances can be set up, one for each zone, and it will be necessary, therefore, to make a further assumption regarding one of these unknowns. The one that will be approximated is the temperature of the combustion gases and this will be done by assuming that the temperature difference between the gas and the stock, which is 220°C where the stock enters the kiln, will be the same at the other end of the preheating zone where the stock is 1110°C , thus making the gas temperature 1330°C at this point. This assumption means that there will be a nearly constant temperature difference between gas and stock throughout this zone, thus assuring a substantially uniform rate of rise of the temperature of the stock which is one of the requirements of this kiln. Of course, there will be an unavoidable but minor deviation from this requirement owing to the heat effect of dehydration.

Call the mols of fuel gas per hour x , and the mols of *excess* air y , and take 20°C as the reference temperature. From the equation



there will be x mols CO_2 , $2x$ mols H_2O , and $2x(79/21) = 7.52x$ mols N_2 as the theoretical products of combustion of x mols of methane, and to this must be added y mols of excess air. The equation for the heat balance in the combustion zone may be worded as follows:

$$\begin{aligned} & \left[\begin{array}{l} \text{Sensible heat recov-} \\ \text{ered by preheating} \\ \text{air in cooling zone} \end{array} \right] + \left[\begin{array}{l} \text{heat of combus-} \\ \text{tion of } x \text{ mols of} \\ \text{natural gas} \end{array} \right] \\ &= \left[\begin{array}{l} \text{sensible heat content of} \\ \text{theoretical products of} \\ \text{combustion above } 20^{\circ}\text{C} \end{array} \right] + \left[\begin{array}{l} \text{heat consumed in heat-} \\ \text{ing stock and car from} \\ 1110 \text{ to } 1210^{\circ}\text{C} \end{array} \right] + \left[\begin{array}{l} \text{wall loss} \\ \text{in this} \\ \text{section} \end{array} \right] \end{aligned}$$

Using the lower heating value for methane (see Table 3-4), the heat input is $103,000 + 345,400x$ Btu/hr, assuming for the time being that the radiation loss in this zone is 8000 Btu/hr per foot of length.

The sensible-heat content above 20°C of the gases leaving the combustion zone is found by taking the number of mols of each gas and multi-

plying by the average molal heat capacity (Fig. 1-3) and by the number of degrees above 20°. These calculations are summarized in the following table:

Gas	Mols	$Mc_{p,av}^{\circ}$ to 1330°C = 2426°F	Temp. diff. °F	Product, mols $\times Mc_{p,av}^{\circ} \times \Delta t$, Btu
CO ₂	x	12.4	2358	29,200 x
N ₂ O.....	$2x$	9.7	2358	45,800 x
N ₂ (theor.).....	7.52 x	7.7	2358	138,200 x
Excess air.....	y	7.77	2358	18,320 y
Total.....	10.52 x	213,200 x
	+ y	+18,320 y

The average specific heat of the stock and car between 1110 and 1210°C is $0.20 + 0.0001(1110 + 1210)/2 = 0.316$, and the heat supplied to the material is $(7630/4)(1210 - 1110)(1.8)0.316 = 108,500$ Btu/hr.

The remaining item of heat output is the radiation loss,

$$8000(15) = 120,000 \text{ Btu/hr}$$

Setting up the equation for the heat balance in the combustion zone, one obtains the following expression:

$$103,000 + 345,400x = 213,200x + 18,320y + 108,500 + 120,000$$

This reduces to $132,200x - 18,320y = 125,500$.

To assist in visualizing this problem, reference may be made to Fig. 12-1, which shows the three separate zones of the kiln considered as separate problems for the purpose of obtaining heat balances. Values on the diagram are original data, assumed values, and figures readily obtained from the original data.

A second equation is obtained from the preheating zone. In this zone the sole source of heat is the sensible-heat content of the hot gases at 1330°. This has already been computed. The heat output consists of that necessary to heat the stock and car from 20 to 1110°C, the sensible heat left in the gases at 240°C, and the radiation loss.

Although the stock loses its combined water over the range from 600 to 700°C, it is assumed for the purpose of simplifying calculations that the original stock is heated to 650°C; decomposition then takes place at this temperature, and the dehydrated material is heated to 1110°C.

Average specific heat of stock, 20 to 650°C:

$$0.22 + 0.00012(650 + 20)/2 = 0.26$$

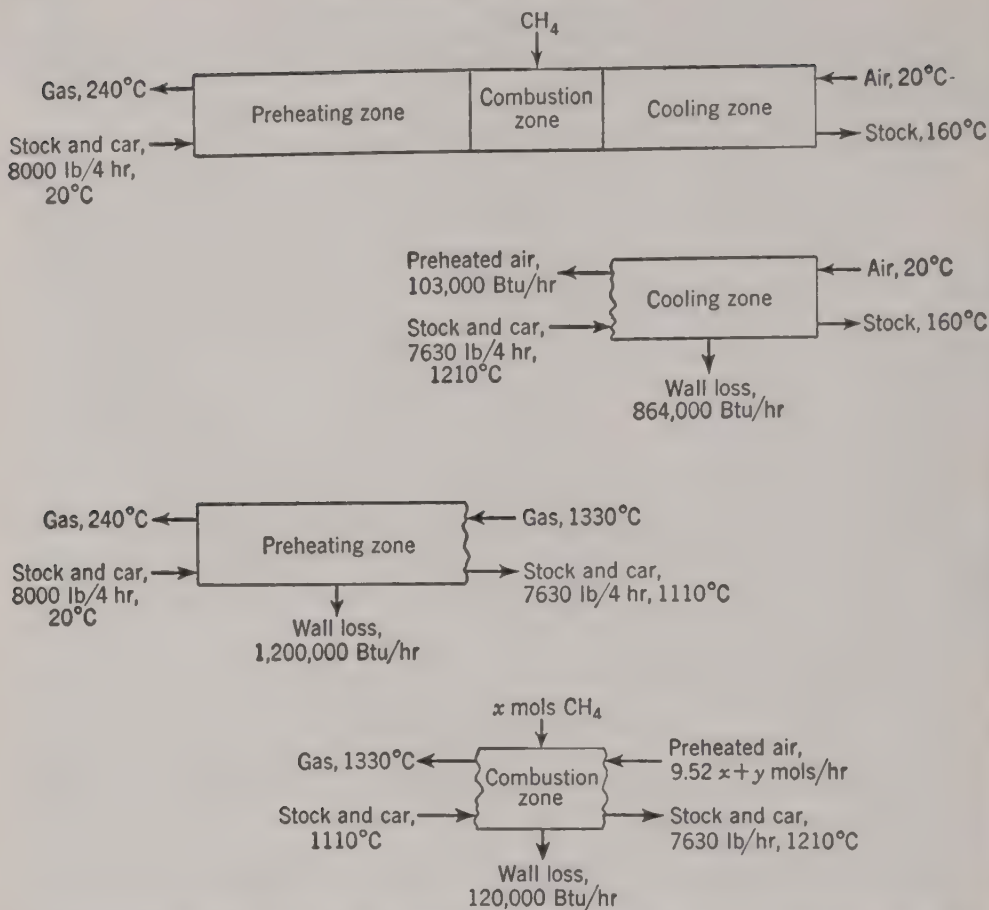


FIG. 12-1. Tunnel kiln fired with natural gas. Radiation loss in preheating and combustion zones = 8000 Btu/hr per foot of length. Solution gives $x = 8.32$ mols CH₄ per hour, $y = 53.1$ mols excess air per hour.

Heat absorbed by original stock, 1500 lb/hr, 20 to 650°C:

$$1500(650 - 20)(1.8)0.26 = 443,000 \text{ Btu/hr}$$

Heat of decomposition, which was estimated at 15 kcal (15,000 cal) per gram mol of combined water, is 15,000 Chu per pound mol of water.

Lb stock per hour	Lb combined H ₂ O	Mols H ₂ O	Chu	
1500	0.062	18	15,000	1.8
				= 139,500 Btu/hr

Average specific heat of stock, 650 to 1110°C:

$$0.20 + 0.0001(1110 + 650)/2 = 0.288$$

Heat absorbed by dehydrated stock, 650 to 1110°C:

$$0.938(1500)(1110 - 650)(1.8)0.288 = 336,000 \text{ Btu/hr}$$

Average specific heat of refractory, 20 to 1110°C:

$$0.20 + 0.0001(1110 + 20)/2 = 0.2565$$

Heat absorbed by refractory, 500 lb/hr, 20 to 1110°C:

$$500(1110 - 20)(1.8)0.2565 = 252,000 \text{ Btu/hr}$$

There is also a small amount of heat to be credited against the heat consumption as calculated above, since the combined water, which is evolved at 650°C, mixes with the gases of combustion and is cooled with them to 240°C. Its average molal heat capacity in this range will be somewhat greater than that obtained for 650°C, or 1200°F, from Fig. 1-3, which uses a base temperature of 60°F, but since the amount involved is small, no great error is introduced by taking the value from Fig. 1-3.

Lb stock/hr	Lb H ₂ O	Mols H ₂ O	Chu/°C	Chu	
1500	0.062		8.75	650-240	1.8
		18			

$$= 33,400 \text{ Btu/hr}$$

Summarizing the heat effects of the stock and car,

	Btu
Heat absorbed by the stock, 20 to 650°C.....	443,000
Heat of decomposition.....	139,500
Heat absorbed by stock, 650 to 1110°C.....	336,000
Heat absorbed by refractory, 20 to 1110°C.....	252,000
Total absorbed.....	1,170,500
Heat recovered by cooling water vapor.....	33,400
Net heat absorbed by stock and car.....	1,137,100

The second item of heat output, which is the sensible-heat content of the gases at 240°C, is calculated as before.

Gas	Mols	$M_{c_{p,av}}^{\circ}$ to 240°C = 464°F	Temp. diff., °F	Product, mols $\times M_{c_{p,av}}^{\circ} \times \Delta t$, Btu
CO ₂	x	9.82	396	3,890 x
H ₂ O	$2x$	8.2	396	6,500 x
N ₂ (theor).....	7.52 x	7.0	396	20,850 x
Excess air.....	y	7.03	396	2,780 y
Total	10.52 x	31,240 x
	+ y	+2,780 y

Radiation loss in this zone, $8,000(150) = 1,200,000 \text{ Btu/hr}$

The equation for the heat balance in the preheating zone may now be written, the heat input being taken from the combustion-zone calculations.

$$213,200x + 18,320y = 1,137,100 + 31,240x + 2,780y + 1,200,000$$

which reduces to

$$181,960x + 15,540y = 2,337,100$$

The combustion zone equation was $132,200x - 18,320y = 125,500$. Solution of these simultaneous equations gives

$$x = 8.32 \text{ mols fuel gas per hour}$$

and

$$y = 53.1 \text{ mols excess air per hour}$$

For the case that radiation loss is one-half as much, or 4000 Btu per foot of length in the combustion and preheating zones and 3200 in the cooling zone, the wall loss in the cooling zone is 432,000 Btu/hr. Since the heat input to this zone from the hot stock and car remains the same, or 967,000 Btu/hr, the heat picked up by the incoming air will be 535,000 Btu/hr.

As before, call the mols of fuel gas per hour x' and the mols of excess air y' . This gives for the combustion zone a heat input of

$$535,000 + 345,400x'$$

The heat output to the gases is $213,200x' + 18,320y'$; that to the stock is 108,500; and the radiation loss at half the former value is 60,000, all values in Btu/hr. The heat balance for this zone becomes

$$132,200x' + 366,500 = 18,320y'$$

For the preheating zone, the heat input is $213,200x' + 18,320y'$. The heat output items are 1,137,100 Btu/hr to stock and car,

$$31,240x' + 2780y' \text{ Btu/hr}$$

to waste gases, and 600,000 Btu/hr to radiation loss. These figures give the heat balance in this zone as $181,960x' + 15,540y' = 1,737,100$. Solution of the two heat-balance equations in x' and y' gives

$$x' = 4.85 \text{ mols fuel gas per hour}$$

and

$$y' = 55.0 \text{ mols excess air per hour}$$

These results should be compared with the results for high radiation loss to appreciate their significance. Consider the first case with high radiation loss. To burn 8.32 mols of CH_4 requires 16.64 mols of oxygen, or $16.64(100/21) = 79.4$ mols of air. The per cent excess air in this case is $(53.1/79.4)100 = 67\%$. With half the radiation loss, fuel consumption

is reduced nearly in proportion, actually to $(4.85/8.32)100 = 58.3\%$ of its value in the former case. However, 4.85 mols of fuel require

$$4.85(2)(100/21) = 46.1 \text{ mols}$$

of air for combustion. The excess air has increased to

$$(55.0/46.1)100 = 119\%$$

but the absolute number of mols of excess air, 55.0 against 53.1, remains substantially constant. This must be so, for in the preheating zone 1,137,100 Btu/hr must be absorbed by the stock whatever the heat loss. The heat supply to this zone as sensible heat in the hot gases is 2,742,000 and 2,041,000 Btu/hr, respectively, for the two cases. The large quantity of heat absorbed by the stock, 41.5% and 55.6% in the two cases, necessitates the presence of a large amount of gas to "throw the heat forward in the kiln" and this in turn means that use of a large (absolute) number of mols of excess air.

Returning to the cooling zone, one can obtain information on the temperature of the preheated air from the figures. In the case of high radiation loss, 103,000 Btu are recovered by the air. Since $79.4 + 53.1 = 132.5$ mols of air are used in the combustion, $103,000/132.5 = 778$ Btu are absorbed per mol if all the air is passed through the cooling zone. As the average molal heat capacity of air in the temperature range involved is about 7.0, the air is heated 111 Fahrenheit degrees, *i.e.*, to a temperature of about 82°C. When the radiation loss is halved, the heat recovered is 535,000 Btu and the air used is $46.1 + 55.0 = 101.1$ mols. This gives a heat absorption of 5290 Btu per mol, meaning that the final temperature of the air is about 430°C.

The conviction that to secure furnace efficiency excess air should be suppressed to the lowest point compatible with good combustion is so widespread that it is worthwhile to analyze the factors that play a part in the furnace the very design of which demands a large air excess. The first factor is the necessity of uniformity of rate of heating of the stock, requiring, as mentioned above, what is called "throwing the heat forward in the kiln." The only thing that can carry heat to the stock before it reaches the combustion zone is hot gas, the heat available depending on the quantity and temperature of that gas. The initial temperature of the gas should be kept down, however, as otherwise at the hot end of the preheating zone the temperature differences between gas and stock will be excessive and the danger both of too rapid heating and of localized overheating correspondingly great. The difficulty due to such excessive and variable temperature differences can be met, as is sometimes done, by resort to indirect heating through flues, but where direct contact between combustion gases and the stock is allowable, it

is cheaper and better to secure uniformity of heating by using excess air. By this method it is easy to secure any desired ratio of the temperature differences at the two ends of the preheating zone and hence meet any required heating schedule, relatively fast at the start and slow at the end, or vice versa, or uniform throughout.

There are whole ranges of operation of such a kiln, however, in which excess air is essential to secure reasonable thermal efficiency, entirely irrespective of heating schedule. With a wall loss of 8000 Btu/(ft)(hr) of the total heat supplied to this kiln in the fuel, 75% is lost through the walls. As already shown, this leaves almost no recoverable heat in the cooling zone. If, on the other hand, this loss be reduced by using more and better insulation, more recoverable heat is available, which will be picked up by the incoming air. Obviously, this air cannot be preheated above the temperature of the hot stock. If now the wall loss be thus reduced to about 60% of the total heat input, theoretical air is insufficient to absorb this recoverable heat, and if a proper excess air be not used to absorb it, thermal efficiency will go down. Furthermore, the percentage excess required gets larger the more efficient the kiln. This applies to all furnaces preheating air by recovering sensible heat from the charge.

It is instructive to consider the limiting case of no radiation loss. The heat requirements for stock and car remain the same. If equations are set up similar to the above, solution shows 1.39 as the mols of gas required, and 57.0 mols of excess air. This is equivalent to 430% excess air. If the *total* air for this case absorbed all the heat given up by the stock in the cooling zone, it would be preheated to over 1000°C. Hence, in this extreme case it is obvious that *theoretical* air could not possibly absorb the efficiently recoverable heat.

The second part of the design is the recalculation of the above figures so that flue requirements, etc., may be modified to take care of the different gas volumes when a lower grade of fuel is used, namely, cold producer gas of the composition 7% CO₂, 21% CO, 15% H₂, 1% CH₄, and 56% N₂. The heat requirements of the stock and radiation losses are the same as before, so these need not be recalculated. For this gas the heat of combustion per mol is different from that of methane, and so also is the theoretical air necessary for combustion.

Consider 1 mol of this fuel. Using the lower heating values for the combustible gases present, the heating value for the fuel is found to be $0.21(67,636) + 0.15(57,798) + 0.01(191,910) = 24,800$ Chu, or 44,600 Btu.

The oxygen required to burn the CO, H₂, and CH₄ in 1 mol of gas is $(0.21/2) + (0.15/2) + (0.01)2 = 0.20$ mol. This brings in

$$0.20(79/21) = 0.752 \text{ mol N}_2$$

The products of combustion are shown in the following table:

Source	Products of combustion		
	CO ₂	N ₂	H ₂ O
Original gas:			
CO ₂	0.07		
CO.....	0.21		
H ₂			0.15
CH ₄	0.01		0.02
N ₂		0.56	
Air for theoretical combustion.....		0.752	
Total.....	0.29	1.312	0.17

In the combustion zone, let x mols of gas burn with the theoretical air plus y mols of excess air. The heat input (for 8000 Btu loss by radiation per hour per foot of length) is $103,000 + 44,600x$. The heat output to the stock is 108,500 Btu/hr and that for radiation is 120,000 Btu/hr. The sensible heat in the combustion gases is a different function of x and y from the former case. Using the method outlined on page 387, the heat content is $36,160x$ for the theoretical products of combustion and $18,320y$ for the excess air. The heat balance for the combustion zone may be written as $103,000 + 44,600x = 108,500 + 120,000 + 36,160x + 18,320y$.

In the preheating zone the heat input is $36,160x + 18,320y$. The heat output is 1,137,100 Btu/hr for the stock, 1,200,000 for radiation loss, and $5320x + 2780y$ for the combustion gases discharged at 240°C. The heat balance is

$$36,160x + 18,320y = 1,137,100 + 1,200,000 + 5320x + 2780y$$

Solution of these two heat-balance equations gives $x = 64.4$ mols of producer gas per hour and $y = 22.8$ mols of excess air per hour.

Similar equations for a heat loss of 4000 Btu/hr per foot of length give 37.5 mols of producer gas required and 37.3 mols of excess air used.

The required air for 64.4 mols of producer gas is

$$64.4(0.20)(100/21) = 61.3 \text{ mols}$$

and for 37.5 mols of producer gas, 35.7 mols of air are required. In the first case 37% excess air is used, and in the second case the excess is 105%. The total air in the first case is preheated to 118°C, and in the second case to 590°C.

For completeness in comparison it can be shown that, if the radiation loss be reduced to zero, 10.8 mols of producer gas are used requiring 10.3 mols of air and using 51.8 mols of excess air. This excess is 505% of the

theoretical amount. The recoverable heat in the stock would theoretically preheat the total air to approximately 1160°C. This temperature, being within 50 centigrade degrees of the temperature of the stock, could not as a practical matter be reached. While it is not feasible to obtain the indicated heat recovery by preheating air alone, part of it could be recovered in this way and the remainder could be recovered by preheating the producer gas by passing it through separate flues in the cooling zone. It is interesting to note that in this kiln natural gas has no advantage, thermal or otherwise, over producer gas. It would, of course, give more risk of localized overheating.

It is perhaps worthwhile to compute the heat consumption of an ideal kiln, *i.e.*, one in which there are no radiation or conduction losses and the stock and stack gases are completely cooled to the original temperature of stock and air. The total heat required to burn the stock has already been computed, namely,

	<i>Btu</i>
Heat absorbed, 20 to 650°C.....	443,000
Heat of decomposition.....	139,500
Heat absorbed, 650 to 1110°C.....	336,000
Heat absorbed, 1110 to 1210°C.....	108,500
Total.....	1,027,000

In the ideal kiln, however, both burnt stock and water vapor formed by decomposition of the stock are cooled to 20°C, the former from 1210°C yielding 790,000 Btu and the latter 41,000 Btu. Subtracting these two quantities from the above total leaves 196,000 Btu as the minimum possible heat consumption of an ideal furnace. On this basis, the thermal efficiency of the kiln can be computed. In a kiln with no wall loss, the heat efficiency is over 40 per cent, in one with a loss of 4000 Btu/ft/hr it is less than 12 per cent, and in one with a loss of 8000 Btu/ft/hr it is less than 7 per cent.

Table 12-1 brings together for comparison the results in the various cases.

The second type of problem to be illustrated in this chapter involves the design of a large-scale unit from data obtained by laboratory experimentation. Unlike the tunnel-kiln problem, which is representative of continuous operation, the process chosen for an example is carried out batchwise. Sometimes conditions applying to the batch in the laboratory will not apply to the batch in the large plant after operations in the plant get under way. For example, the recycling of partially converted material may change quantities or concentrations of reacting materials and thus affect the size of tanks and reactors needed. Therefore, before the data obtained in the laboratory can be used to calculate the quantities of materials and sizes of vessels required for the process, problems of this

TABLE 12-1. SUMMARY OF CALCULATIONS ON TUNNEL KILN

	Natural gas			Producer gas		
Heat loss, Btu/(ft)(hr) ..	8000	4000	0	8000	4000	0
Mols fuel gas required ..	8.32	4.85	1.39	64.4	37.5	10.8
Mols theoretical air	79.4	46.1	13.2	61.3	35.7	10.3
Mols excess air	53.1	55.0	57.0	22.8	37.3	51.8
Total mols air	132.5	101.1	70.2	84.1	73.0	62.1
Per cent excess air	67	119	430	37	105	505
Total mols stack gas* ..	145.9	111.2	76.8	142	109	76.2
Heat recovered in cooling zone, Btu	103,000	535,000	967,000	103,000	535,000	967,000
Temperature of preheated air, °C	82	430	1045	118	590	1160
Total heat supplied, † Btu	2,875,000	1,675,000	480,000	2,870,000	1,672,000	482,000
Heat loss by radiation, Btu	864,000	432,000	0	864,000	432,000	0
Per cent radiation loss ..	30.0	25.8	0	30.1	25.8	0
Thermal efficiency	6.8	11.7	40.1	6.8	11.7	40.7

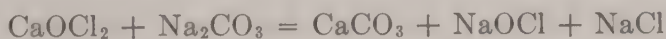
* Including 5.2 mols of water vapor from loss of combined water by stock.

† 345,400x for natural gas and 44,600x for producer gas.

type frequently require the estimation of plant conditions after operations have become stabilized.

DESIGN OF SODIUM HYPOCHLORITE PROCESS

Assume that it be desired to produce a solution of NaOCl from one of CaOCl₂ by precipitation with soda ash according to the reaction



The product is to be decanted from the precipitated CaCO₃ and the precipitate washed three times by decantation, using equal volumes of wash water each time, the combined wash waters being sufficient to make up the next batch. The reason for this is the impracticability of concentrating dilute bleach solutions. The data given in Table 12-2 were taken from a laboratory experiment. A diagram of the process is given in Fig. 12-2.

In this problem, the complication arises from the fact that, in the laboratory, the solution of bleaching powder was made up with water, whereas in the plant wash waters from a previous batch will be used. If such wash waters were available in the laboratory, plant conditions could be simulated. The experiment might be repeated in the laboratory, always maintaining the same concentration of available chlorine in the product in every experiment, until conditions paralleling plant operation

were realized, but this would be a tedious operation and it is easier to compute what these conditions would be. In the first run an amount of bleach had to be used sufficient not only to supply the product but also to make up the hypochlorite carried in process in the wash waters. Hence, the amounts of sludge and of wash waters were unduly large

TABLE 12-2. LABORATORY DATA ON SODIUM HYPOCHLORITE PROCESS

Weight of bleaching powder taken.....	286 g
Weight of water for solution.....	1660 g
Weight of solution.....	1946 g
Specific gravity of solution.....	1.085
Volume of thiosulfate (0.1107 <i>N</i>) for 2-cc sample.....	30.07 cc
Weight of soda ash.....	300 g
Weight of water to dissolve.....	1900 g
Weight of solution.....	2200 g
Specific gravity of solution.....	1.118 g
Volume of HCl (0.1856 <i>N</i>) for 2-cc sample.....	26.42 cc
Calculated soda-ash solution required, assuming bleach = 45% CaO, using 10% excess.....	2060 g
Extra water added.....	45 g
Total weight of mixed solutions.....	4050 g
Depth of original solution.....	8.0 in.
Settling time to 2 in.....	2 hr
Temperature.....	25°C
Volume decanted.....	2760 cc
Volume of sludge.....	924 cc
Volume of thiosulfate for 2 cc of product.....	13.46 cc
Specific gravity of product.....	1.066
Wash water No. 1:	
Specific gravity.....	1.030
Volume.....	1330 cc
Thiosulfate for 2 cc.....	6.03 cc
Wash water No. 2:	
Specific gravity.....	1.020
Volume.....	1340 cc
Thiosulfate for 4 cc.....	5.84 cc
Wash water No. 3:	
Specific gravity.....	1.010
Volume.....	1335 cc
Thiosulfate for 6 cc.....	5.08 cc
Sludge:	
Volume.....	910 cc
Thiosulfate for 4 cc.....	4.01 cc

relative to the product. In the second operation, much less bleach would be used and the sludge and wash waters would be unduly small. Thus, even if the experiment had been repeated in the laboratory, the second run would not have been comparable with balanced plant operation. Finally, however, after a sufficient number of repetitions, say n

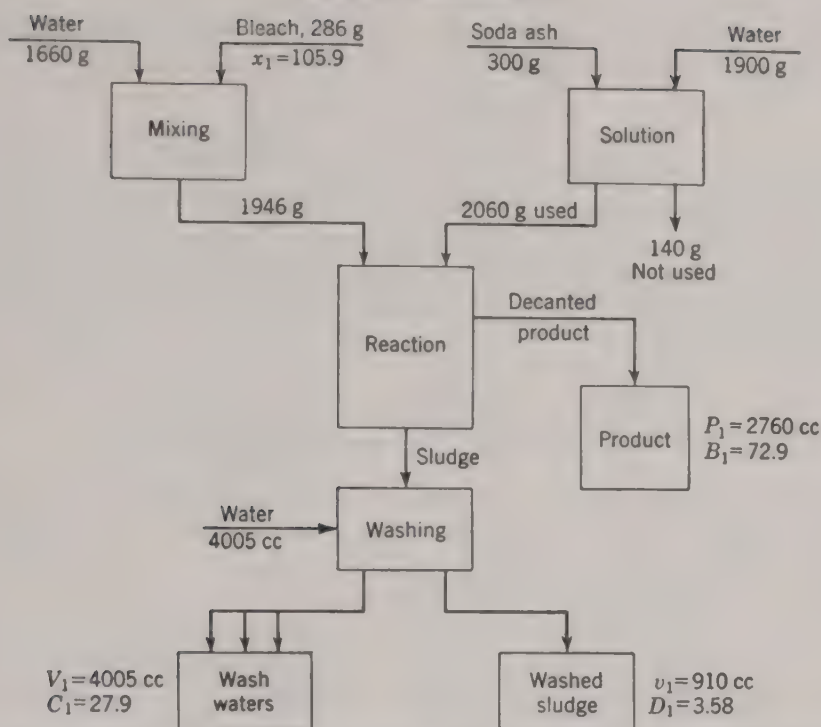


FIG. 12-2. Hypochlorite process. Figures refer to laboratory quantities per batch, first operation. X_1 , B_1 , C_1 , and D_1 are available chlorine calculated from analytical data.

operations, these variations will iron out. Hence, the problem is to compute the conditions that will obtain upon the n th operation.

Solution. The first equation to be written for this process is a material balance. In this problem the balance can be most logically expressed in terms of available chlorine. Therefore, use the following nomenclature:

- X = weight of available chlorine in bleaching powder used per batch
- B = weight of available chlorine in product
- C = weight of available chlorine in combined wash waters
- D = weight of available chlorine left in final sludge
- P = volume of product
- V = total volume of wash waters
- v = volume of sludge

For no chemical loss, $X + C = B + C + D$. However, the laboratory data show a loss of 1.4%, probably due largely to chemical decomposition. Therefore, assuming a constant chemical loss of 1.4% for n th-operation conditions, the material balance is

$$0.986(X + C) = B + C + D \quad (1)$$

To avoid unduly complicated equations, it may be assumed that the

chemical loss applies only to the new bleach. This gives the simpler relationship

$$0.986X = B + D \quad (1a)$$

which will give results for B and X within 0.3% of equation (1).

Next, several relationships can be developed in terms of concentrations. Study of the data shows that the volumetric concentration of available chlorine in the sludge is higher than in the supernatant liquid, perhaps due to adsorption on the sludge. Except for this, the proportion could be written

$$\frac{\text{Available Cl in sludge}}{\text{Available Cl in solution}} = \frac{\text{volume of sludge}}{\text{volume of solution}} \quad (2)$$

In this expression the term "solution" could refer either to the supernatant liquid or to the sum of sludge and supernatant liquid. One method of taking into account the excess chlorine in the sludge is to use a factor α , assumed constant, such that

$$\frac{\text{Available Cl in sludge}}{\text{Available Cl in s.n. liquid}} = \alpha \frac{\text{volume of sludge}}{\text{volume of s.n. liquid}} \quad (3)$$

This may be altered by the rules of proportion to the form

$$\frac{\text{Available Cl in sludge}}{\text{Available Cl in (sludge + s.n. liq.)}} = \frac{\alpha (\text{vol. sludge})}{\alpha (\text{vol. sludge}) + \text{vol. s.n. liq.}} \quad (4)$$

The factor α may be evaluated in several ways. Using the laboratory data for the final sludge and the third wash water in the proportion (2) gives $\alpha = 1.19$. This value is probably less reliable than one computed from the more concentrated solutions, such as the stronger wash waters or the product. Since no data are given from which to make a direct calculation, the following analytical approach is used. The subscript 1 denotes first-operation laboratory conditions; the absence of a subscript indicates final or n th-operation conditions, which are assumed to be carried out on a comparable laboratory scale under such conditions as will produce the same concentration of available chlorine in the product.

After decantation of the product in the laboratory, the chlorine left behind in the first sludge was $C_1 + D_1$. Since the volume of water¹ used for each wash is $V/3$, the chlorine left behind in the sludge after the first wash is obtainable from proportion (4) as

$$(C_1 + D_1) \left(\frac{\alpha v_1}{\alpha v_1 + V/3} \right)$$

¹ This assumes that the volume of the solution is equal to the volume of water from which it is made.

After the second wash it is

$$(C_1 + D_1) \left(\frac{\alpha v_1}{\alpha v_1 + V/3} \right)^2$$

and after the third wash it is

$$(C_1 + D_1) \left(\frac{\alpha v_1}{\alpha v_1 + V/3} \right)^3 = D_1 \quad (5)$$

Solving this expression, $\alpha = 1.37$. Since this value has been obtained from a relationship that takes into account all the washings, it is more characteristic of the process than the value of 1.19, which was obtained from consideration only of the last washing.

Now consider the distribution proportion (2) applied to the decantation of product from the first sludge

$$\frac{C_1 + D_1}{B_1} = \frac{\alpha v_1}{P_1}$$

Substituting the laboratory data in this expression gives $\alpha = 1.29$. Considering all three values, the use of an average of 1.3 for α should give results that are correct to within 5% except for the final washing.

For n th-operation conditions, the following equations are available:

$$0.986X = B + D \quad (1a)$$

$$\frac{C + D}{B} = \frac{\alpha v}{P} \quad (2)$$

$$(C + D) \left(\frac{\alpha v}{\alpha v + V/3} \right)^3 = D \quad (5)$$

A fourth equation makes the ratio of the sludge in the n th operation to that in the first equal to the ratio of the bleach added in the n th to the bleach used in the first. This relationship must hold granting constant conditions of precipitation and decantation. That is,

$$v/v_1 = X/X_1 \quad (6)$$

Basis for Solution. To solve these equations—four equations containing seven unknowns—a basis for solution must be selected and reasonable assumptions must be made as to relationships between various quantities. Since n th operation must produce the same concentration of available chlorine in the product as the first operation, *i.e.*,

$$P/B = P_1/B_1$$

the most logical basis is to take $P = P_1$, and $B = B_1$. For a first trial it may be assumed that the loss of available chlorine in the final sludge

is the same percentage of the new bleach used as it was in the first operation, *i.e.*, $D = 0.0338X$, which is obtainable from laboratory data. This leads to

$$B = 0.952X$$

The various quantities computed by means of the preceding equations are shown in Table 12-3.

TABLE 12-3. *n*TH-OPERATION QUANTITIES IN SODIUM HYPOCHLORITE PROCESS

First operation	Quantity	<i>n</i> th operation	
		First trial	Second trial
72.9 g	Chlorine in product, $B = B_1$	72.9 g	72.9 g
2,760 cc	Volume of product, $P = P_1$	2,760 cc	2,760 cc
105.9 g	Chlorine in new bleach, $X = B/0.952$	76.6 g	75.94 g
3.58 g	Chlorine in final sludge, $D = 0.0338X$	2.6 g	1.97 g
910 cc	Volume of final sludge, $v = v_1(X/X_1)$	658 cc	653 cc
27.9 g	Chlorine in wash waters, C	20.0 g	20.2 g
4,005 cc	Volume of wash waters, V	2,718 cc	3,180 cc

In the "first-trial" figures, the quantity of wash waters V is calculated from C , D , α , and v by Eq. (5). It will be noted that 2718 cc of wash water is not enough to dissolve the bleach and soda ash and get 2760 cc of product plus 658 cc of sludge. Consequently, more water is needed. This can be added to the batch as water, or it can be added as wash water, thus decreasing the loss of chlorine in the sludge. Assume that the latter choice is made and that for a second trial $D = 0.026X$. Recalculation gives the values in the last column of Table 12-3. These values are shown on Fig. 12-3, which is the diagram for *n*th-operation conditions.

The reasonableness of 3180 cc as the value for V can be checked by getting the ratio of water to bleach in each case. In the laboratory experiment 3485 cc of water were used for 105.9 g of available Cl in the bleach, a ratio of 33.0. In the "first trial" figures, the ratio is

$$2718/(76.6 + 20.0) = 28.1$$

assuming that the water used is approximately equal to the wash water produced. In the "second trial" figures, the ratio is

$$3180/(75.94 + 20.2) = 33.1$$

which is close enough to 33.0 to be a check.

The calculations are continued to get the quantities of materials used. The results are summarized in Table 12-4 and are shown on Fig. 12-3.

TABLE 12-4. *n*TH-OPERATION QUANTITIES—CONTINUATION OF TABLE 12-3

First operation	Quantity	<i>n</i> th operation
105.9 g	Weight of available Cl in bleach	75.94 g
286 g	Weight of bleaching powder	205 g
1790 cc	Volume of solution	1280 cc
300 g	Soda ash weighed out	
281 g	Soda ash actually used, $(2060/2200)(300)$	
	Soda ash actually used, $(75.94/105.9)(281)$	201 g
1843 cc	Volume of actual solution	
45 cc	Volume of water added	3180 cc
3678 cc	Sum of volumes	3180 cc
2760 cc	Volume of product	2760 cc
924 cc	Volume of sludge	653 cc
3684 cc	Sum of volumes	3413 cc

Assume that this process is to be carried out in a plant operating to produce a product containing 1000 lb of available chlorine and that it is required to calculate the various quantities of chemicals and volumes of

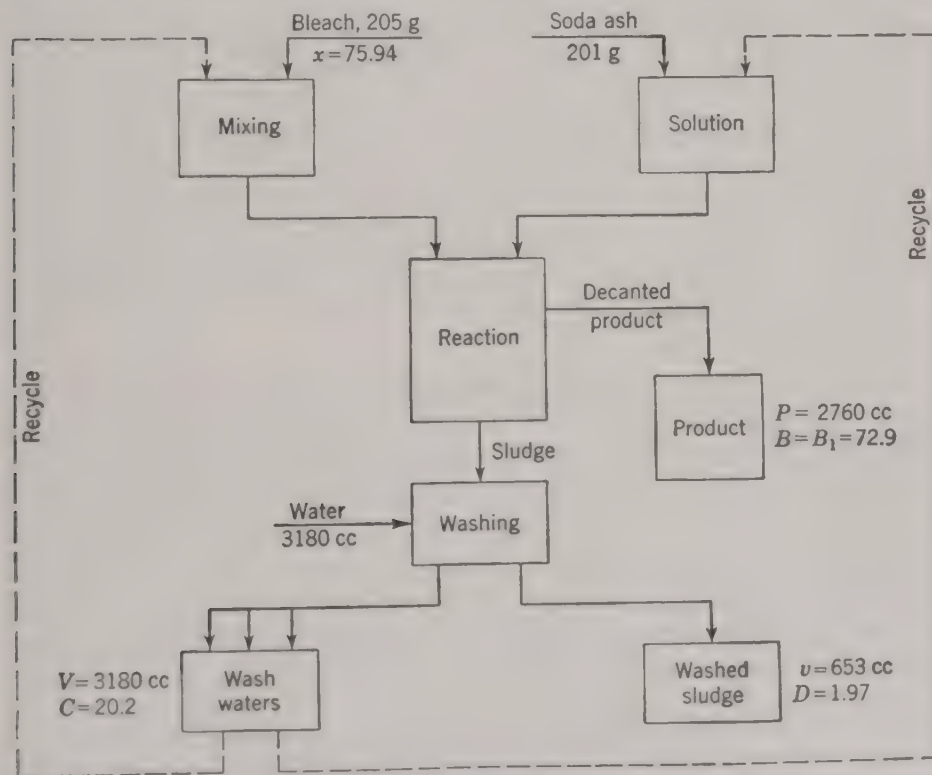


FIG. 12-3. Hypochlorite process, *n*th-operation laboratory quantities per batch. Second trial calculations, basis $B = B_1 = 72.9$. X , B , C , and D are available chlorine for *n*th-operation conditions.

solutions. There are many ways of making the required conversion from metric to English units and from small to large scale, but the following is one of the easiest to visualize.

The n th-operation laboratory experiment would use 205 g of bleaching powder, 201 g of soda ash, and 3180 cc of wash waters to give a combined volume of 3413 cc, of which 2760 cc would be product and 653 cc would be sludge. Since a cubic centimeter is the volume of a gram of water, the expression "gram-volume" might be used in place of it. Thus, the laboratory-scale process would use 205 g of bleaching powder, 3180 "gram volumes" of wash waters, etc.

Imagine a new experiment performed using the same process in a hypothetical plant but starting with 205 lb of bleaching powder and 201 lb of soda ash. The product of this experiment would contain 72.9 lb of available chlorine.

To get the volumes involved in plant-scale operations, many chemists and engineers employ for this type of calculation a unit of volume called the "pound-volume," so that ratio of volume to mass will have the same numerical values in the English system of units as in the metric system. The "pound-volume," abbreviated as pv, is defined as the volume occupied by 1 lb of water at standard temperature and pressure. Thus, 3180 "pound-volumes" of wash waters would be required, and there would be produced 2760 "pound-volumes" of product and 653 "pound-volumes" of sludge which, combined, would occupy 3413 "pound-volumes." Thus, all figures for the experiment conducted in pounds would be numerically equal to the figures for the corresponding materials in grams, and the advantage of the term "pound-volumes" is to extend the identity of numerical values to volumetric quantities.¹ Pound-volumes may be converted into gallons or cubic feet by dividing respectively by 8.33 pv/gal and 62.4 pv/cu ft.

The plant is required, however, to produce 1000 lb of available chlorine per batch, which is $1000/72.9 = 13.7$ times the size of the hypothetical plant scale. Hence, the scale of the plant, in both weight and volume, is 13.7 times as large. Table 12-5 repeats many of the data of Table 12-4 and includes a third column of figures based on a product containing 1000 lb of available chlorine.

A little practice will enable one to discard the second column of figures when making calculations of this kind. Doing so is equivalent to making the conversion by the following sort of proportion. If 205 g of bleach-

¹ The reader will recognize that the pound-volume has the same advantage when making volumetric calculations that the Chu has in thermal calculations. The former maintains the same numerical value of the ratio of volume/mass in the English system as obtains in the metric system, while the latter makes it possible to maintain the same numerical value for the ratio of heat/mass in both systems.

ing powder yields a product containing 72.9 g of available chlorine, then X lb of bleach will yield a product containing 1000 lb of available chlorine, i.e., $205 \text{ g}/72.9 \text{ g} = X \text{ lb}/1000 \text{ lb}$; $X = (205/72.9)1000 \text{ lb} = 2815 \text{ lb}$. Similarly, $3180 \text{ cc}/72.9 \text{ g} = Y \text{ pv}/1000 \text{ lb}$;

$$Y = (3180/72.9)1000 \text{ pv} = 43,650 \text{ pv}$$

The method of working the problem by proportion is entirely legitimate, but it is necessary to pay careful attention to the units involved. In the first proportion the units cancel; in the second proportion, the units on the left are cubic centimeters per gram, which have the same numerical value as the units on the right, which are pound-volumes per pound. It

TABLE 12-5. CONVERSION OF LABORATORY QUANTITIES TO PLANT-SCALE OPERATIONS

	Laboratory, nth operation	Equivalent data in English units	Full-scale plant
Available Cl in product.....	72.9 g	72.9 lb	1000 lb
Weight of bleach required.....	205 g	205 lb	2815 lb
Weight of soda ash.....	201 g	201 lb	2760 lb
Volume of recycled wash water.....	3180 cc	3180 pv	43,650 pv
Same, gal.....	5250 gal
Water used per wash.....	1750 gal
Volume of batch.....	3413 cc	3413 pv	46,900 pv
Same, gal.....	5640 gal
Volume of product.....	2760 cc	2760 pv	37,900 pv
Same, gal.....	4550 gal
Specific gravity of this solution.....	1.066	1.066	1.066
Weight of product.....	2940 g	2940 lb	40,400 lb
Volume of sludge.....	653 cc	653 pv	8950 pv
Same, cu ft.....	143.5 cu ft

is thus seen that the ratio $1000/72.9 = 13.7$ is a sort of conversion factor that can be used on either weights or volumes, to convert grams on the laboratory scale to pounds in the plant, or cubic centimeters in the laboratory to pound-volumes in the plant.

It is obvious that equipment must be provided of ample capacity and strength to handle the volumes and weights thus computed, including adequate allowance for factors such as splashing, frothing, and the like.

It will be noted that in the laboratory experiment the input was 105.9 g of available chlorine. However, 27.9 g were recovered in the wash waters, leaving, after crediting this, a net input of 78.0 g. The product contained 72.9 g, and the loss was therefore 5.1 g. Of this, 3.6 g were accounted for in the sludge because of incomplete washing, and the remainder, 1.5 g, was caused by decomposition and other losses. The

percentage loss was therefore $100(5.1/78.0) = 6.54\%$, and the percentage chlorine efficiency was 100 minus this, or 93.46%. On the other hand, it was shown above that under *n*th-operation conditions the total percentage loss is 4.0%, only 61% as great as the laboratory loss. The corresponding chemical efficiency of the *n*th operation is 96.0%. This higher efficiency is due to the fact that, when part of the chlorine in process is returned in the wash waters from the previous batch, the volume of sludge is lessened, since the wash waters contain no calcium to be precipitated. The smaller sludge is washed more completely by the available wash waters, and the loss is thereby reduced. It is essential to keep in mind the fact that, whenever material is recovered from a process for recycling, the efficiency realized in the laboratory does not represent that to be anticipated in the plant, but must be corrected for this recycling effect. However, recycling does not always result in an increase in efficiency over that of the laboratory.

While the calculations involved in the above design are lengthy, the principles on which they are based are simple. Essentially, the conditions of the *n*th operation are determined by material balances, together with equations expressing the distribution of components between various streams and other characteristic features of the process. As with methods developed in other chapters, application of these principles can be made to both inorganic and organic chemical technology.

PROBLEMS

1.* The electrolytic process for the production of magnesium involves primarily the electrolysis of dehydrated magnesium chloride. A typical process for preparation of the anhydrous MgCl_2 for use in the cell involves the use of a brine containing approximately 14% NaCl , 9% CaCl_2 , 3% MgCl_2 , and 0.5% bromine. After the bromine is removed, the brine is treated with magnesium hydrate slurry to precipitate the iron and other impurities, which are separated in continuous thickeners and sedimentation tanks. The decanted liquor is then evaporated until the NaCl has crystallized. The salt is removed. The MgCl_2 and CaCl_2 are then separated from each other by fractional crystallization. After a series of crystallizations, approximately one-half of the MgCl_2 originally present in the brine has been removed, the other half being returned to the process for reworking. The final steps in preparing feed for the electrolytic cell consist in a series of dehydration operations to remove the six molecules of water of crystallization, which correspond to 53% of the weight of the hydrated flaked chloride. There is a complete series of hydrated salts containing, respectively, six, four, two, and one molecules of H_2O . Air-drying on the countercurrent principle is practical to a composition corresponding approximately to $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, provided the temperature is carefully controlled to prevent incipient fusion. The last two molecules of water are removed by heating to still higher temperature in an atmosphere of HCl , which is necessary to prevent hydrolysis and the formation of MgO .

(a) Sketch a flow sheet showing all steps in the preparation of anhydrous MgCl_2 from the brine.

* Problem based on 1943 Student Contest Problem of the American Institute of Chemical Engineers.

(b) Calculate the weights of all streams (volumes for gases) required to produce 1 ton of product.

(c) Calculate per ton of product the Btu that must be supplied to evaporate the mixed chlorides and crystallize the NaCl .

(d) Calculate per ton of product the Btu that must be supplied in the air-drying operation to get $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$.

2. A method of concentrating waste sulfite liquor has been described by J. N. Franklin and H. O. Goddard.¹ It consists of "borrowing" boiler steam at 200 to 250 psig and using it to concentrate waste liquor containing about 10% solids in a converter, or evaporator, and producing a concentrated liquor containing 50% solids and acid steam at 100 psig. Then this acid steam is fed to the steam side of a secondary steam converter while the boiler steam condensate from the first converter, originally at high pressure, is fed to the liquid side of the secondary converter where it is converted to low-pressure steam (30 to 50 psig) which is "returned" to the plant for process work.

In a pilot plant built to test the first step in the operation, the following information was obtained:

Feed, 2.27 U.S. gallons per minute at 136°F containing 9.6% solids.

Boiler steam at 230 psig, 1270 lb/hr.

Acid steam produced at 100 psig.

Concentrate at 100 psig led off to a flash chamber and flashed to atmospheric pressure. Final concentration of solids = 55%.

(a) Make a complete heat balance on this unit and continue the heat balance to show what will happen in the secondary converter where the acid steam at 100 psig is used to convert the boiler-steam condensate back into steam at 30 psig. Assume no boiling-point rise due to solids in the waste liquor.

(b) Estimate the high-pressure steam consumption and the low-pressure steam make for a plant concentrating 2,500,000 lb of waste sulfite liquor (equivalent to 100 tons of sulfite pulp).

(c) What can you say of the "thermal efficiency" of this process?

(d) What is your opinion of the choice of 100 psig as the intermediate pressure? Would you recommend that a higher or a lower pressure be used?

3. An oil contains 60% of naphthalene contaminated with light oil and heavy oil. In a batch still equipped with a 17-plate fractioning column, a 10,000-gal charge is run off with the following products: first fraction, 800 gal containing 90% of light oil and 10% of naphthalene; second fraction, 1800 gal of intermediate containing 60% of naphthalene and 40% of light oil; third fraction, 4850 gal of "refined" naphthalene which is 96% pure, the impurities being 2% each of light oil and heavy oil. The balance is distillation residue. It takes 3 hr to charge the still and get the distillate running and $1\frac{1}{4}$ hr to pump out the residue. During the production period the total vapor upflow in the column is kept reasonably constant at 2100 gal/hr. When making the light fraction and intermediate, the forward flow is 160 gal/hr, and when making the 96% naphthalene fraction, it averages 360 gal/hr. Thus, the total time to make a run on a fresh charge is 34 hr. These seem to be about the best operating conditions with the present equipment. The light fraction, 96% naphthalene fraction, and residue are salable products, but the intermediate must be charged back into the still for the next run.

It is desired to estimate n th-operation conditions on this still on the basis of charging back the intermediate from a run into the next run. It is known that:

1. The still charge cannot exceed 10,000 gal.
2. The total vapor flow cannot exceed 2100 gal/hr.

¹ *Pulp & Paper Mag. Can.*, 51 (3), 139 (1950).

3. The forward-flow rates during light and intermediate fractions are not to exceed 160 gal/hr, and during the 96% naphthalene fraction they are not to exceed 360 gal/hr.

4. The production of intermediate, which is a characteristic of the crude, the equipment, and the way it is operated, will remain the same for each run.

(a) On the basis of your analysis what is the annual capacity of this still for oil of the same quality as that now being refined?

(b) It is proposed to add 10 plates to the fractionating column in order to improve its efficiency. It will be run at the same rates as now, but the improved efficiency will be used for reducing the size of the intermediate fraction to 500 gal and for reducing the naphthalene content of the residue to 5%. Estimate first-run and *n*th-operation conditions with the new equipment on the same basis as before.

What is the annual capacity of the new equipment? Compare the annual production of refined naphthalene on the new equipment with that on the old.

(c) The accounting department sometimes uses a simplified method of figuring costs, which is to take the total annual charges against the still and divide by the number of hours operated during the year. On this basis the cost of a "still-hour" on the old equipment is \$7.10. Assuming that the cost of a still-hour remains the same for the new equipment, approximately how much can be saved annually by adding the 10 plates if the quantity of crude oil to be processed annually remains the same as at present?

4. A drier for MnSO_4 solution was made from a piece of standard 12-in. pipe 5 ft long.¹ The solution being dried contained approximately 20% MnSO_4 , 2% MgSO_4 , and 0.5% FeSO_4 . The optimum operation involved evaporating 750 ml/min of solution, which produced about 20 lb/hr of solid product, which was discharged at about 500°C in an anhydrous condition. In the pipe, the following zones could be observed: the first 24 to 30 in. remained wet and no solids formed; in the next 12 to 18 in. violent boiling occurred; the last 10 to 12 in. contained only dried product.

A typical survey of the temperature in the middle of the gas stream was as follows:

Distance from combustion chamber, in.	0	12	30	48	60
Temperature, °C.	950	600	510	400	300

Speed of rotation was about 4 rpm; the product was continually pushed along the horizontal tube with rakes.

Heat was supplied by combustion of 200 to 250 cu ft/hr of 800-Btu gas. The solution was evaporated at the rate of 11.9 gal/hr. It is stated that the thermal efficiency of the drier was 55 to 70% and that a longer tube, well insulated at the hot end, would improve the efficiency.

Compared with an evaporator followed by a drier, this rotary drier is more suitable. It is simpler and less expensive, although the fuel costs are greater.

(a) Get a heat balance on each section of this drier and interpret it.

(b) Estimate the effect of adding insulation and redesign the pilot-scale drier to develop improved efficiency resulting from insulation.

(c) Design an economical drier of this type to produce 10 tons/day of pure MnSO_4 from a 20% solution. Give length, diameter, and cubic feet of gas required. Base the design on the assumption that the heat transfer is proportional to the surface area of the drier and not to volume as in an ordinary rotary kiln.

5. A pilot plant for production of potassium metaphosphate is described by Copson, Pole, and Baskervill² and is shown in Fig. 12-4.

¹ U.S. Bur. Mines Rept. Invest. 3609 (January, 1942).

² R. L. Copson, G. R. Pole, and W. H. Baskervill, *Ind. Eng. Chem.*, **34**, 26 (1942).

The normal operation was as follows: Phosphorus, melted under hot water, was burnt with the proper amount of air to maintain a temperature of 1000 to 1050°C in the combustion chamber and 800 to 900°C in the reaction chamber. A commercial grade (60 to 61% of K_2O) of fine potassium chloride (98% minus 14 mesh) was blown in by means of small air jets at the top of the reaction chamber at the proper rate to give the desired P_2O_5/K_2O ratio in the product. Water was added at the top of the packed tower, and part of the phosphorus pentoxide was collected as acid in the tower. The partially reacted potassium chloride and the acid from the tower fell into the

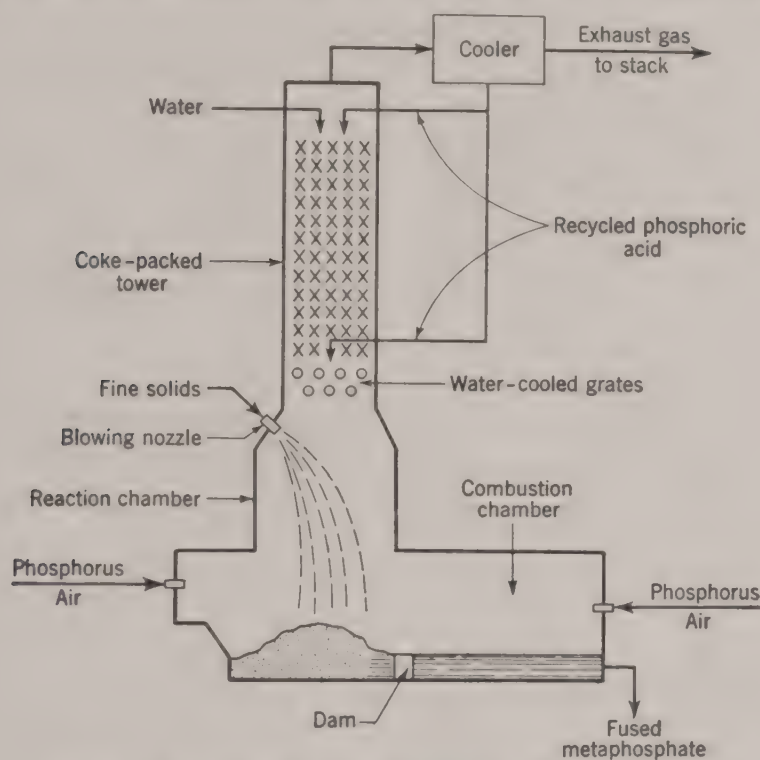


FIG. 12-4. Pilot plant for production of metaphosphates.

furnace, where the reaction was completed. The gases left the packed tower at about 100°C and then passed to the cooler, where they were cooled to 70 to 80°C before going to the hydrochloric acid recovery system. The recovered phosphoric acid from the cooler was returned to the packed tower above the water-cooled grate. The molten product collected in the combustion chamber, and was tapped from the furnace every 2 hr into a water-cooled steel pan, where it was left to solidify. Data obtained from a run of 78 hr, in which 14 tons of potassium metaphosphate were produced, are given below.

Phosphorus (99.2% P_4) burnt, tons/day.....	1.27
KCl (61.3% K_2O) charged, tons/day.....	2.64
K metaphosphate (58% P_2O_5 , 35% K_2O , 1.8% Cl_2) produced, tons/day.....	4.31
Recovery of phosphorus as K metaphosphate, %.....	87
Recovery of potassium as K metaphosphate, %.....	93
Volatilization of chlorine as HCl, %.....	94

The coke-packed tower and the cooler of the pilot plant were not completely effective in preventing losses of phosphorus pentoxide and of potassium, as the data show. Undoubtedly improvements could be made in the recovery system that would increase the yield of potassium metaphosphate. The recovery of hydrochloric acid was not studied quantitatively, although it was found that the hydrochloric acid contained small percentages of phosphoric acid and potassium chloride.

It is desired to make a study of the pilot-plant process preliminary to the design of a full-scale plant.

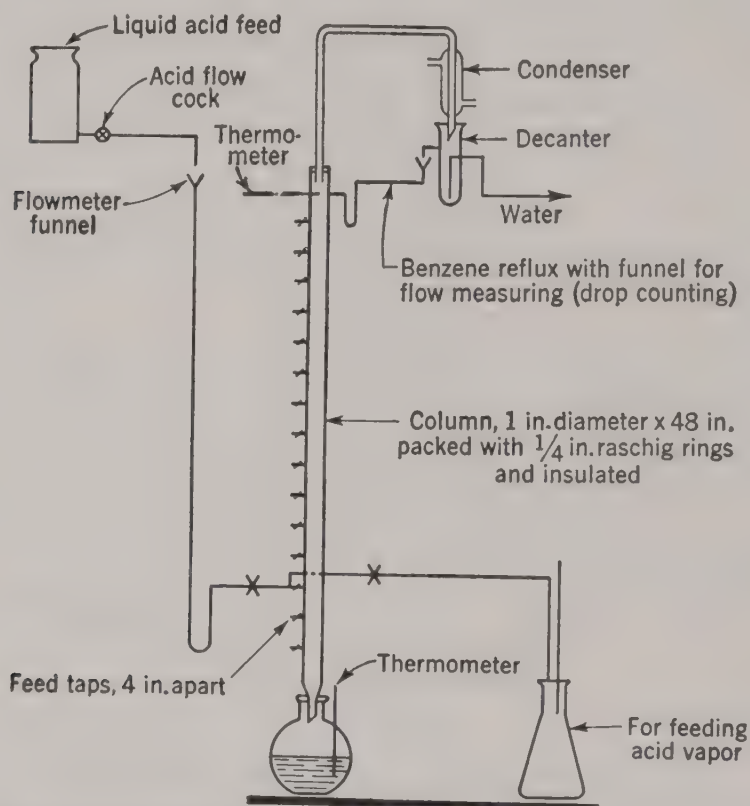


FIG. 12-5. Laboratory apparatus for continuous nitration of benzene.

(a) Estimate the temperature of the combustion gases from burning phosphorus with the theoretical amount of air. Estimate the per cent of excess air used in the pilot plant.

(b) If the combustion gases were cooled from 800 to 100°C in the packed tower entirely by water injected at the top, how much water would be used? (In this calculation neglect H_3PO_4 formation.) How does this amount of water compare with the theoretical amount required for the process?

(c) If 150% of the theoretical water required by the process were sprayed in at the top of the coke tower and were all vaporized, how much heat must be removed from the gases entering the coke tower either by cooling water or by radiation loss to cool them from 800 to 100°C?

(d) What is the composition of the gases that must be handled by the HCl-recovery system?

6. The continuous nitration of benzene has been studied by Othmer, Jacobs, and Levy,¹ who used a laboratory apparatus like that shown in Fig. 12-5. Results of three test runs using vapor feed of nitric acid are given in the following table:

CONTINUOUS NITRATION OF BENZENE USING NITRIC-ACID VAPOR

	Run number		
	40	41	42
Rate of feed, g/min.....	5.83	5.83	1.52
Total acid feed, g.....	700.0	706.0	111.0
Time, min.....	119.0	120.0	120.0
Benzene charged, g.....	918.0	992.0	971.0
Temp. of vapors at top of column, °C.....	73	76	72
Temp. of pot, °C.....	82	82	82
Per cent of acid feed going to pot			
Water layer.....	9.8	8.7	7.8
Benzene layer.....	21.2	18.7	14.0
Per cent of acid feed going to decanter			
Water layer.....	6.2	7.3	6.0
To benzene reflux.....	0.0	1.0	0.2
Per cent of acid feed converted to nitrobenzene.....	61.0	64.0	63.0
Per cent of benzene charged			
Going to pot.....	47.2	46.0	76.8
Going to reflux.....	14.7	15.2	16.1
Converted to nitrobenzene.....	35.0	34.0	8.5
Per cent unaccounted for			
Acid.....	1.8	0.3	0.9*
Benzene.....	3.1	4.8	1.4*
Rate of benzene reflux, g/min.....	5.0	20.0	5.0
Ratio, benzene-reflux/acid-feed.....	0.863	3.44	3.29

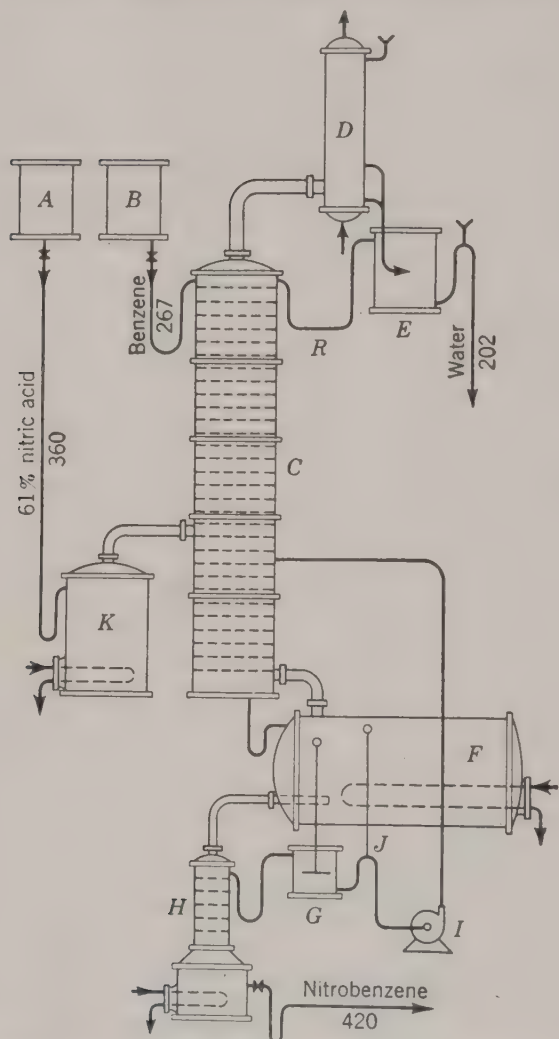
* Sum of products greater than sum of reactants, owing to analytical errors.

Based on these data, a plant to make 5 tons/day of nitrobenzene was designed as shown in Fig. 12-6. In this process, 61% nitric acid is delivered continuously from storage tank *A* to vaporizer *K* and then introduced as vapor into column *C*, where it comes in contact with benzene. The latter is supplied to the top of the column from storage tank *B* or as reflux of recovered benzene from decanter *E*. The reacted material flows to the distilling kettle *F*. The liquid products from kettle *F* overflow to a decanter *G*, which separates an aqueous nitric acid layer from the nitrobenzene-benzene layer. The aqueous nitric acid layer is recycled to the column by means of pump *I*. The nitrobenzene-benzene layer containing some dissolved nitric acid overflows from the decanter into a small distilling column *H* used for stripping the benzene and any nitric acid from the nitrobenzene product. If the available steam pressure used in the heater for column *H* is inadequate to make nitrobenzene (bp, 208°C) at the base of the column, a satisfactory product is one that contains 5% benzene (bp, 118°C) from which the benzene can be removed later by steam distillation.

¹ D. F. Othmer, J. J. Jacobs, Jr., and J. F. Levy, *Ind. Eng. Chem.*, **34**, 286 (1942).

(a) Check all quantities (pounds of material flowing per hour) given in Fig. 12-6. Calculate the flow rates of vapor and liquid in all lines for which rates are not given.

(b) Calculate the amount of nitric acid recycled by pump *I* on the assumptions that in the more efficient full-scale column the amount of nitric acid going to the decanter *E* is negligible and that the percentage conversion of nitric acid per pass down the column is the same as in the laboratory runs.



- A. Nitric-acid storage (61 per cent HNO_3).
- B. Benzene storage.
- C. Nitrating column (approximately 30 inches in diameter).
- D. Hot condenser.
- E. Decanter for separating hot benzene and water condensate.
- F. Distilling kettle with heating coils for steam.
- G. Decanter for separating the nitric acid and benzene-nitrobenzene layers leaving the distilling kettle.
- H. Distilling column for separating benzene and dissolved nitric acid from nitrobenzene, equipped with base heater.
- I. Pump for recycling nitric acid and water layer back to nitrating column.
- J. Vent line to distilling kettle.
- K. Nitric acid vaporizer.

FIG. 12-6. Flow sheet for nitration of benzene to nitrobenzene in plant having a capacity of 5 tons per day of nitrobenzene. (Figures refer to pounds of material flowing per hour.)

(c) If the vapor leaving the top of column *C* corresponded to that from the constant boiling mixture of benzene and water, how much benzene reflux would flow through line *R*? Compare this quantity with the operating conditions used in runs 40 and 41.

(d) If the benzene feed and benzene reflux are cold (25°C), what is the quantity and composition of the vapors entering the top plate of the column from below? What should be the diameter of the column if the vapors entering the top plate are to have a maximum velocity of 1 ft/sec? Compare your result with the size recommended.

(e) Estimate the heating load for each piece of heat-transfer equipment.

APPENDIX

TABLE A-1. EQUIVALENTS AND CONVERSION FACTORS

	English units	Metric units
Length:		
1 mile.....	5280 ft	
1 foot.....	12 in.	30.48 cm
1 inch.....		2.54 cm
Volume:		
1 gallon.....	231 cu in.	
1 cubic foot.....	7.48 gal	28.3 liters
1 pound-molecular volume (gas).....	359 cu ft at 32°F, 1 atm	
1 gram-molecular volume (gas).....		22.4 liters at 0°C, 1 atm
Mass:		
1 pound.....		454 gm
1 short ton.....	2000 lb	
1 long ton.....	2240 lb	
1 gallon of water.....	8.33 lb	
1 cubic foot of water.....	62.4 lb	
Pressure:		
1 atmosphere.....	14.7 lb/sq in.	760 mm Hg
1 atmosphere.....	29.9 in. Hg	
Temperature:		
1 centigrade degree.....	1.8 Fahrenheit degrees	
Conversion factors:		
Degrees Fahrenheit = 1.8 (°C) + 32.....		
Degrees centigrade = (°F - 32)/1.8.....		
Degrees Kelvin (°K) = °C + 273.....		
Degrees Rankine (°R) = °F + 460.....		
Heat:		
1 centigrade heat unit (Chu).....	1.8 Btu	454 cal
1 British thermal unit (Btu).....		252 cal

TABLE A-2. PHYSICAL CONSTANTS OF CHEMICAL SUBSTANCES*

Substance	Formula	Boiling point (1 atm), °C	Critical properties	
			T_c , °C	p_c , atm
Acetone.....	C_3H_6O	56.5	235.0	47.0
Acetylene.....	C_2H_2	-84†	36.0	62.0
Air.....			-140.7	37.2
Ammonia.....	NH_3	-33.4	132.4	111.5
Aniline.....	C_6H_7N	184.4	426	52.4
Benzene.....	C_6H_6	80.1	288.5	47.7
<i>n</i> -Butane.....	C_4H_{10}	-0.6	153.	36.0
<i>n</i> -Butanol.....	$C_4H_{10}O$	117	287	48.4
Carbon dioxide.....	CO_2	-78.5†	31.1	73.0
Carbon monoxide.....	CO	-192	-139.0	35.0
Carbon tetrachloride.....	CCl_4	76.8	283.1	45.0
Chlorine.....	Cl_2	-34.6	144.0	76.1
Cyclohexane.....	C_6H_{12}	80-81	281.0	40.4
Ethane.....	C_2H_6	-88.6	32.1	48.8
Ethanol.....	C_2H_5OH	78.4	243.1	63.1
Ethylene.....	C_2H_4	-103.9	9.7	50.9
Helium.....	He	-268.9	-267.9	2.26
<i>n</i> -Hexane.....	C_6H_{14}	69	234.8	29.5
Hydrogen.....	H_2	-252.7	-239.9	12.8
Hydrogen chloride.....	HCl	-85	51.4	81.6
Hydrogen sulfide.....	H_2S	-59.6	100.4	88.9
Isobutane.....	C_4H_{10}	-10	134.0	37.0
Isopentane.....	C_5H_{12}	27.95	187.8	32.8
Mercury.....	Hg	356.9	> 1550	> 200
Methane.....	CH_4	-161.4	-82.5	45.8
Methanol.....	CH_3OH	64.7	240.0	78.7
Methyl chloride.....	CH_3Cl	-24	143.1	65.8
Nitric oxide.....	NO	-151	-94.0	65.0
Nitrogen.....	N_2	-195.8	-147.1	33.5
Nitrous oxide.....	N_2O	-90.7	36.5	71.7
<i>n</i> -Octane.....	C_8H_{18}	125.7	296.0	24.6
Oxygen.....	O_2	-183	-118.8	49.7
<i>n</i> -Pentane.....	C_5H_{12}	36.3	197.2	33.0
Phenol.....	C_6H_5OH	181.4	419.0	60.5
Propane.....	C_3H_8	-42.2	96.8	42.0
Propylene.....	C_3H_6	-48	92.3	45.0
Pyridine.....	C_5H_5N	115-116	344.0	60.0
Sulfur dioxide.....	SO_2	-10.0	157.2	77.7
Sulfur trioxide.....	SO_3	44.6	218.3	83.6
Toluene.....	$C_6H_5CH_3$	110.8	320.6	41.6
Water.....	H_2O	100	374.15	218.4

* J. H. Perry (ed.), "Chemical Engineers' Handbook," 3d ed., pp. 110, 129, 204, McGraw-Hill Book Co., Inc., New York, 1950.

† Sublimes.

TABLE A-3. SATURATED STEAM: TEMPERATURE TABLE*

Temp., deg F	Absolute pressure		Specific volume, cu ft/lb		Enthalpy, Btu/lb		
	lb/sq in.	In. Hg 32°F	Sat. liquid	Sat. vapor	Sat. liquid	Latent heat	Sat. vapor
32	0.0886	0.1806	0.01602	3305.7	0	1075.1	1075.1
34	0.0961	0.1957	0.01602	3060.4	2.01	1074.0	1076.0
36	0.1041	0.2120	0.01602	2836.6	4.03	1072.9	1076.9
38	0.1126	0.2292	0.01602	2632.2	6.04	1071.7	1077.7
40	0.1217	0.2478	0.01602	2445.1	8.05	1070.5	1078.6
42	0.1315	0.2677	0.01602	2271.8	10.06	1069.3	1079.4
44	0.1420	0.2891	0.01602	2112.2	12.06	1068.2	1080.3
46	0.1532	0.3119	0.01602	1965.5	14.07	1067.1	1081.2
48	0.1652	0.3364	0.01602	1829.9	16.07	1065.9	1082.0
50	0.1780	0.3624	0.01602	1704.9	18.07	1064.8	1082.9
52	0.1918	0.3905	0.01603	1588.4	20.07	1063.6	1083.7
54	0.2063	0.4200	0.01603	1482.4	22.07	1062.5	1084.6
56	0.2219	0.4518	0.01603	1383.5	24.07	1061.4	1085.5
58	0.2384	0.4854	0.01603	1292.7	26.07	1060.2	1086.3
60	0.2561	0.5214	0.01603	1208.1	28.07	1059.1	1087.2
62	0.2749	0.5597	0.01604	1129.7	30.06	1057.9	1088.0
64	0.2949	0.6004	0.01604	1057.1	32.06	1056.8	1088.9
66	0.3162	0.6438	0.01604	989.6	34.06	1055.7	1089.8
68	0.3388	0.6898	0.01605	927.0	36.05	1054.5	1090.6
70	0.3628	0.7387	0.01605	868.9	38.05	1053.4	1091.5
72	0.3883	0.7906	0.01606	814.9	40.04	1052.3	1092.3
74	0.4153	0.8456	0.01606	764.7	42.04	1051.2	1093.2
76	0.4440	0.9040	0.01607	718.0	44.03	1050.1	1094.1
78	0.4744	0.9659	0.01607	674.4	46.03	1048.9	1094.9
80	0.5067	1.032	0.01607	633.7	48.02	1047.8	1095.8
82	0.5409	1.101	0.01608	595.8	50.02	1046.6	1096.6
84	0.5772	1.175	0.01608	560.4	52.01	1045.5	1097.5
86	0.6153	1.253	0.01609	527.6	54.01	1044.4	1098.4
88	0.6555	1.335	0.01609	497.0	56.00	1043.2	1099.2
90	0.6980	1.421	0.01610	468.4	58.00	1042.1	1100.1
92	0.7429	1.513	0.01611	441.7	59.99	1040.9	1100.9
94	0.7902	1.609	0.01611	416.7	61.98	1039.8	1101.8
96	0.8403	1.711	0.01612	393.2	63.98	1038.7	1102.7
98	0.8930	1.818	0.01613	371.3	65.98	1037.5	1103.5
100	0.9487	1.932	0.01613	350.8	67.97	1036.4	1104.4
102	1.0072	2.051	0.01614	331.5	69.96	1035.2	1105.2
104	1.0689	2.176	0.01614	313.5	71.96	1034.1	1106.1
106	1.1338	2.308	0.01615	296.5	73.95	1033.0	1107.0
108	1.2020	2.447	0.01616	280.7	75.94	1032.0	1107.9
110	1.274	2.594	0.01617	265.7	77.94	1030.9	1108.8
112	1.350	2.749	0.01617	251.6	79.93	1029.7	1109.6
114	1.429	2.909	0.01618	238.5	81.93	1028.6	1110.5
116	1.512	3.078	0.01619	226.2	83.92	1027.5	1111.4
118	1.600	3.258	0.01620	214.5	85.92	1026.4	1112.3

* Abridged version of steam tables as published by Combustion Engineering, Inc.

TABLE A-3. SATURATED STEAM: TEMPERATURE TABLE* (Continued)

Temp., deg F	Absolute pressure		Specific volume, cu ft/lb		Enthalpy, Btu/lb		
	lb/sq in.	In. Hg 32°F	Sat. liquid	Sat. vapor	Sat. liquid	Latent heat	Sat. vapor
120	1.692	3.445	0.01620	203.47	87.91	1025.3	1113.2
122	1.788	3.640	0.01621	193.18	89.91	1024.1	1114.0
124	1.889	3.846	0.01622	183.46	91.90	1023.0	1114.9
126	1.995	4.062	0.01623	174.28	93.90	1021.8	1115.7
128	2.105	4.286	0.01624	165.72	95.90	1020.7	1116.6
130	2.221	4.522	0.01625	157.57	98.89	1019.5	1117.4
132	2.343	4.770	0.01626	149.85	99.89	1018.3	1118.2
134	2.470	5.029	0.01626	142.61	101.89	1017.2	1119.1
136	2.603	5.300	0.01627	135.75	103.88	1016.0	1119.9
138	2.742	5.583	0.01628	129.28	105.88	1014.9	1120.8
140	2.887	5.878	0.01629	123.18	107.88	1013.7	1121.6
142	3.039	6.187	0.01630	117.39	109.88	1012.5	1122.4
144	3.198	6.511	0.01631	111.90	111.88	1011.3	1123.2
146	3.363	6.847	0.01632	106.74	113.88	1010.2	1124.1
148	3.536	7.199	0.01633	101.84	115.87	1009.0	1124.9
150	3.716	7.566	0.01634	97.20	117.87	1007.8	1125.7
152	3.904	7.948	0.01635	92.81	119.87	1006.7	1126.6
154	4.100	8.348	0.01636	88.64	121.87	1005.5	1127.4
156	4.305	8.765	0.01637	84.68	123.87	1004.4	1128.3
158	4.518	9.199	0.01638	79.92	125.87	1003.2	1129.1
160	4.739	9.649	0.01639	77.39	127.87	1002.0	1129.9
162	4.970	10.12	0.01640	74.02	129.88	1000.8	1130.7
164	5.210	10.61	0.01642	70.81	131.88	999.7	1131.6
166	5.460	11.12	0.01643	67.78	133.88	998.5	1132.4
168	5.720	11.65	0.01644	64.89	135.88	997.3	1133.2
170	5.990	12.20	0.01645	62.14	137.89	996.1	1134.0
172	6.272	12.77	0.01646	59.52	139.89	995.0	1134.9
174	6.565	13.37	0.01647	57.03	141.89	993.8	1135.7
176	6.869	13.99	0.01648	54.66	143.90	992.6	1136.5
178	7.184	14.63	0.01650	52.41	145.90	991.4	1137.3
180	7.510	15.29	0.01651	50.28	147.91	990.2	1138.1
182	7.849	15.98	0.01652	48.24	149.92	989.0	1138.9
184	8.201	16.70	0.01653	46.30	151.92	987.8	1139.7
186	8.566	17.44	0.01654	44.45	153.93	986.6	1140.5
188	8.944	18.21	0.01656	42.69	155.94	985.3	1141.3
190	9.336	19.01	0.01657	41.01	157.95	984.1	1142.1
192	9.744	19.84	0.01658	39.40	159.95	982.8	1142.8
194	10.168	20.70	0.01659	37.86	161.96	981.5	1143.5
196	10.605	21.59	0.01661	36.40	163.97	980.3	1144.3
198	11.057	22.51	0.01662	35.00	165.98	979.0	1145.0
200	11.525	23.46	0.01663	33.67	167.99	977.8	1145.8
202	12.010	24.45	0.01665	32.39	170.01	976.8	1146.6
204	12.512	25.47	0.01666	31.17	172.02	975.3	1147.3

* Abridged version of steam tables as published by Combustion Engineering, Inc.

TABLE A-3. SATURATED STEAM: TEMPERATURE TABLE* (Continued)

Temp., deg F	Absolute pressure		Specific volume, cu ft/lb		Enthalpy, Btu/lb		
	lb/sq in.	In. Hg 32°F	Sat. liquid	Sat. vapor	Sat. liquid	Latent heat	Sat. vapor
206	13.031	26.53	0.01667	30.01	174.03	974.1	1148.1
208	13.568	27.62	0.01669	28.90	176.04	972.8	1148.8
210	14.123	28.75	0.01670	27.83	178.06	971.5	1149.6
212	14.696	29.92	0.01672	26.83	180.07	970.3	1150.4
215	15.591		0.01674	25.37	183.10	968.3	1151.4
220	17.188		0.01677	23.16	188.14	965.2	1153.3
225	18.915		0.01681	21.17	193.18	961.9	1155.1
230	20.78		0.01684	19.388	198.22	958.7	1156.9
235	22.80		0.01688	17.778	203.28	955.3	1158.6
240	24.97		0.01692	16.324	208.34	952.1	1160.4
245	27.31		0.01696	15.027	213.41	948.7	1162.1
250	29.82		0.01700	13.841	218.48	945.3	1163.8
260	35.43		0.01708	11.771	228.65	938.6	1167.3
270	41.85		0.01717	10.070	238.84	931.8	1170.6
280	49.20		0.01726	8.651	249.06	924.6	1173.7
290	57.55		0.01735	7.465	259.31	917.4	1176.7
300	67.01		0.01745	6.471	269.60	910.1	1179.7
310	77.68		0.01755	5.628	279.92	902.6	1182.5
320	89.65		0.01765	4.915	290.29	895.0	1185.3
330	103.03		0.01776	4.310	300.69	887.1	1187.8
340	117.99		0.01788	3.789	311.14	879.2	1190.3
350	134.62		0.01799	3.342	321.64	871.0	1192.6
360	153.01		0.01811	2.958	332.19	862.5	1194.7
370	173.33		0.01823	2.625	342.79	853.8	1196.6
380	195.70		0.01836	2.336	353.45	844.9	1198.4
390	220.29		0.01850	2.083	364.17	835.7	1199.9
400	247.25		0.01864	1.8632	374.97	826.2	1201.2
420	308.82		0.01894	1.4995	396.78	806.7	1203.5
440	381.59		0.01926	1.2166	418.91	785.9	1204.8
460	466.97		0.0196	0.9941	441.42	763.6	1205.0
480	566.12		0.0200	0.8172	464.37	739.8	1204.2
500	680.80		0.0204	0.6748	487.80	714.2	1202.0
520	848.37		0.0210	0.5338	518.0	679.2	1197.2
550	1045.6		0.0218	0.4239	594.3	640.9	1190.2
575	1275.7		0.0226	0.3369	582.1	597.4	1179.5
600	1543.2		0.0236	0.2668	616.8	548.4	1165.2
650	2208.8		0.0268	0.1616	696.0	422.7	1118.7
700	3094.1		0.0369	0.0758	823.9	171.7	995.6
705.34 **	3206.2		0.0541	0.0541	910.3	0	910.3

* Abridged version of steam tables as published by Combustion Engineering, Inc.

** Critical temperature.

$$\text{Specific heat} = \text{Chu} / (\text{lb.}) (\text{deg. C.}) = \text{B.t.u.} / (\text{lb.}) (\text{deg. F.}) \\ = \text{calories} / (\text{gm.}) (\text{deg. C.})$$

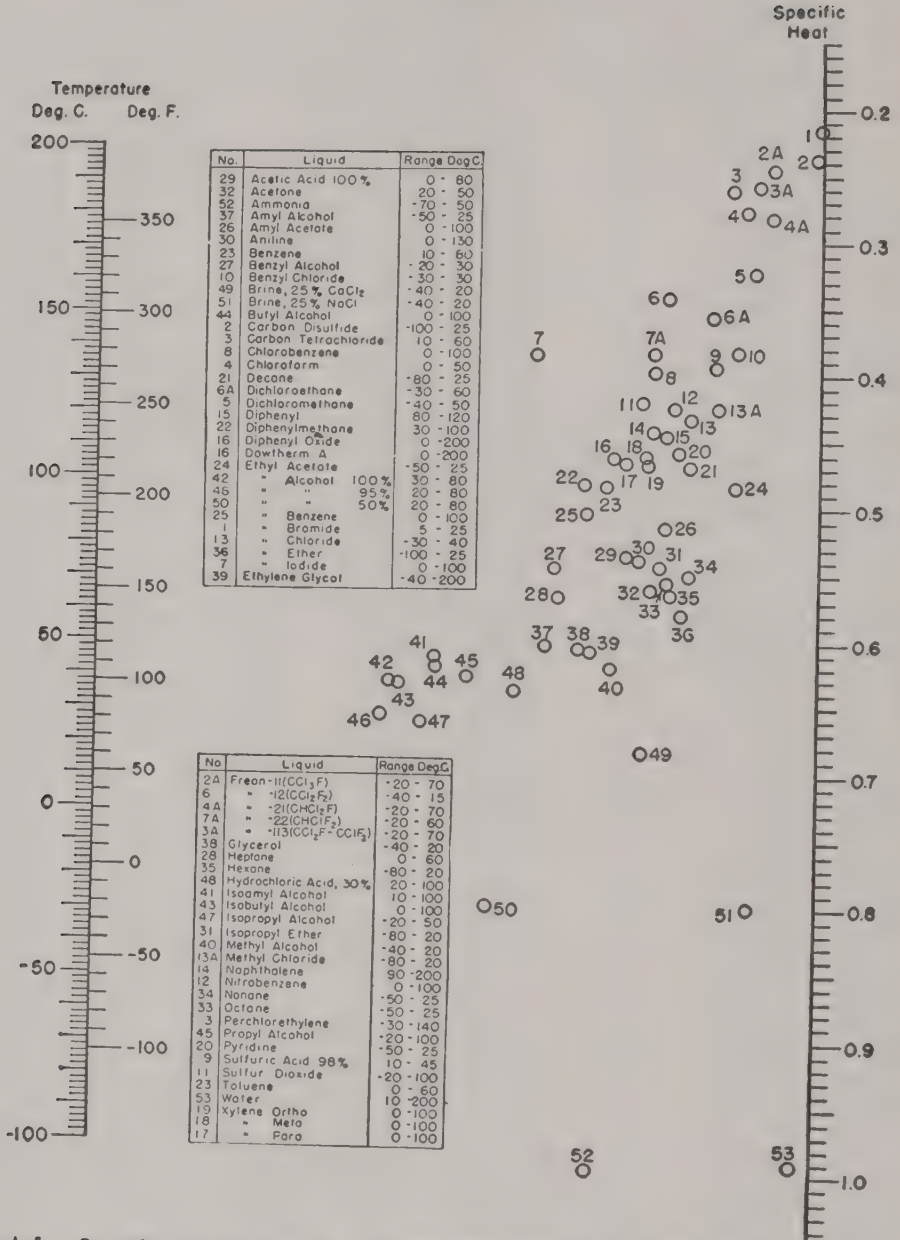


FIG. A-1. Specific heat of liquids. (By permission from J. H. Perry, Chemical Engineers' Handbook, 3d ed., McGraw-Hill Book Company, New York, 1950.)

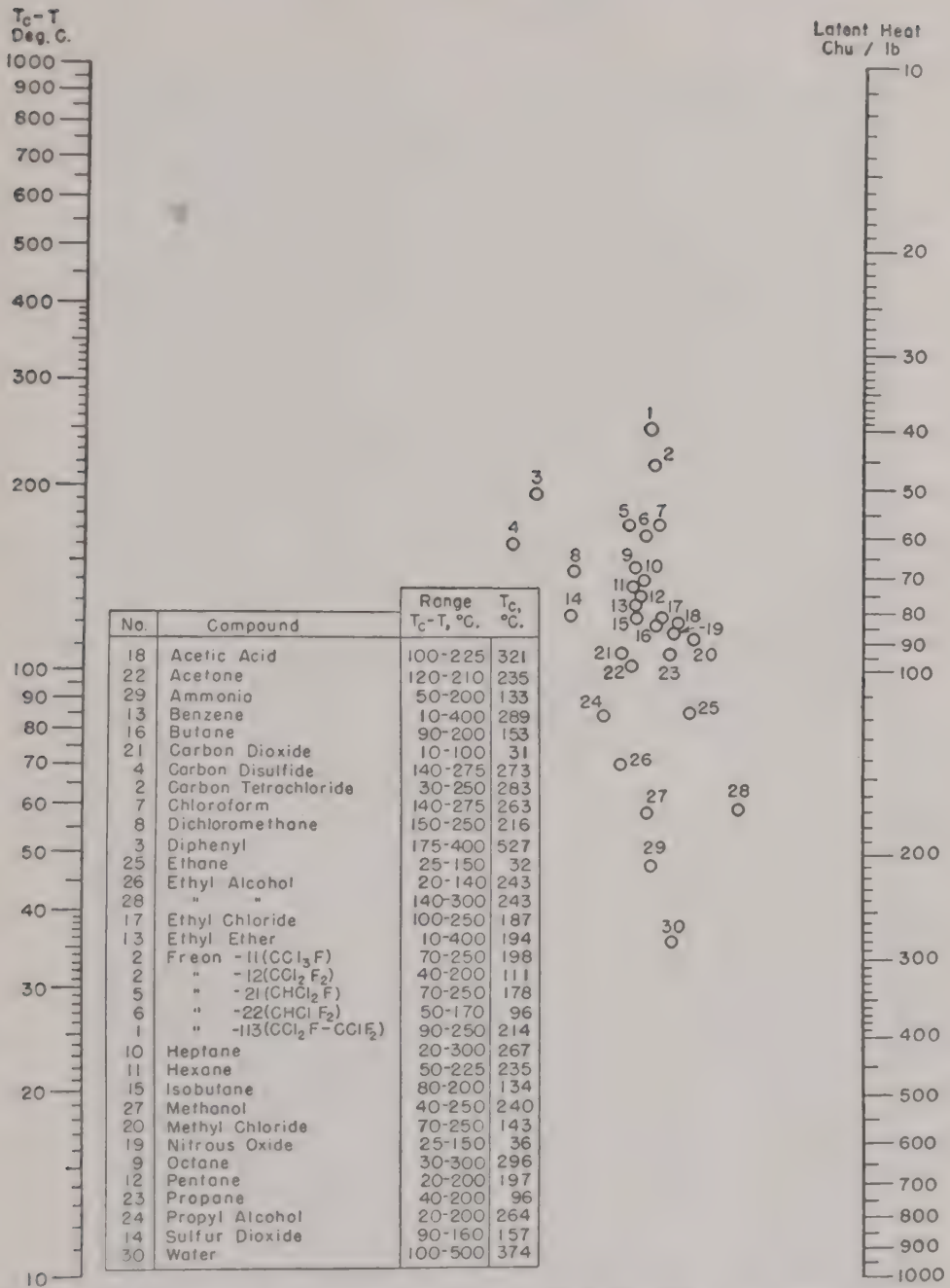


FIG. A-2. Latent heat of vaporization. (By permission from J. H. Perry, *Chemical Engineers' Handbook*, 3d ed., McGraw-Hill Book Company, New York, 1950.)

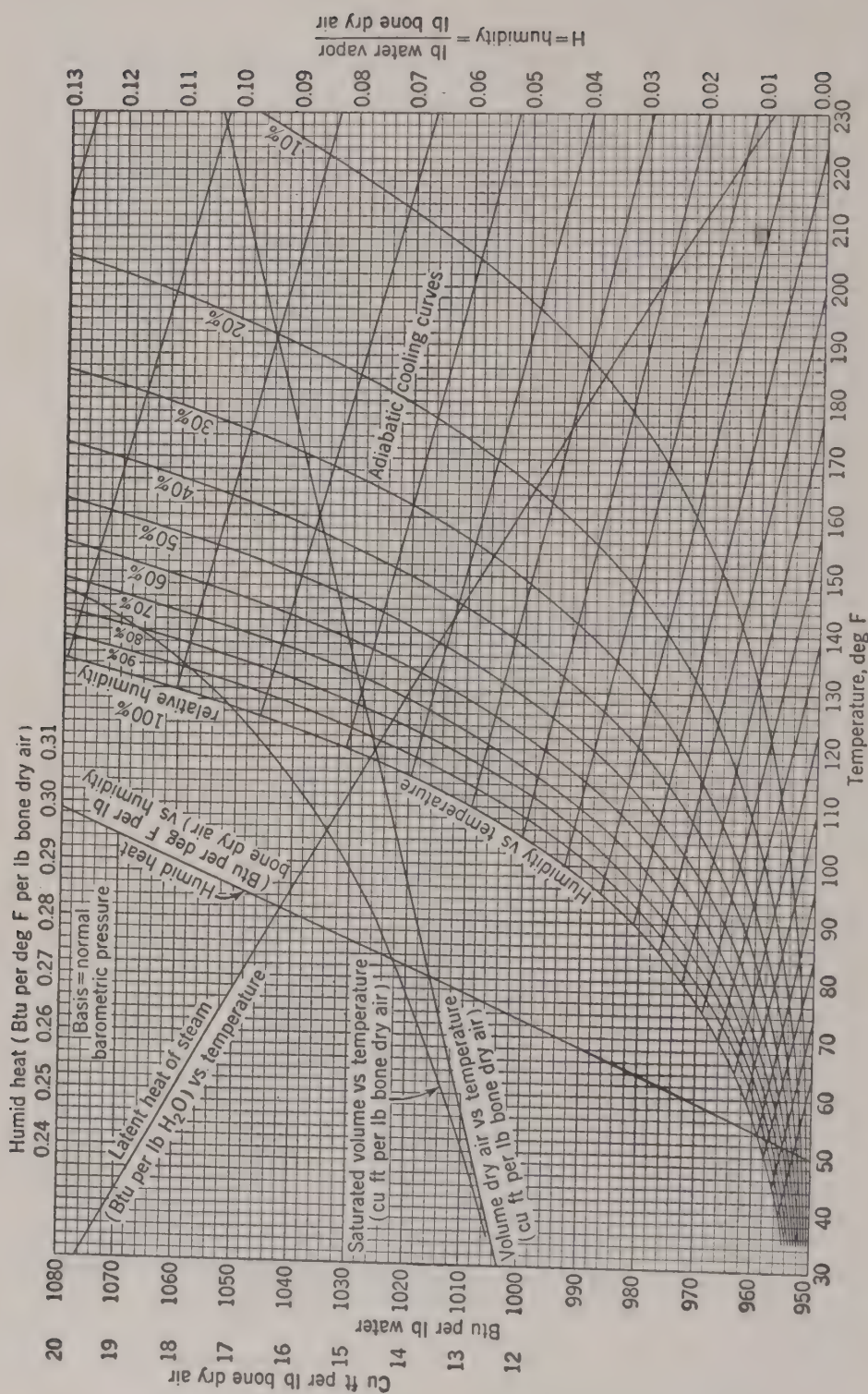


FIG. A-3. Psychrometric chart.

USE OF FIG. A-3 PSYCHROMETRIC CHART

1. *To determine the relative humidity of air from its observed wet-bulb and dry-bulb temperatures.* First locate the intersection of the 100 per cent relative humidity curve and a vertical line through the wet-bulb temperature, read on the abscissa scale. Through this intersection draw a line parallel to the nearest adiabatic cooling curve. The condition of the air is represented by the intersection of this line with a vertical line through the dry-bulb temperature, read on the abscissa scale. For example, if air has a wet-bulb temperature of 90°F and a dry-bulb temperature of 110°F, the first intersection is at $t = 90$, $H = 0.0310$, and the second is at $t = 110$, $H = 0.0262$. The latter point corresponds to a relative humidity of 47 per cent. (For a discussion of the theory involved see W. H. Walker, W. K. Lewis, W. H. McAdams and E. R. Gilliland, "Principles of Chemical Engineering," 3d ed., Chap. 17, McGraw-Hill Book Company, Inc., New York, 1937.)

2. *To determine the percentage absolute humidity of air.* The absolute humidity, $H = \text{lb water vapor/lb bone-dry air}$, of the air in the example chosen was $H = 0.0262$. Saturated air at 110°F has an absolute humidity $H = 0.059$, which is found at the intersection of the vertical line through 110°F and the 100 per cent relative humidity (saturation) curve. Consequently, its percentage absolute humidity was

$$\left(\frac{0.0262}{0.059} \right) 100 = 44 \text{ per cent}$$

Note the difference between this and the relative humidity, which was 47 per cent.

3. *To find the humid volume of air.* First find the volume of dry air at the dry-bulb temperature of the air, then the volume of air saturated with water vapor at this temperature. In the example chosen these values are, respectively, 14.3 and 15.7 cu ft, which are read from the two volume curves where they intersect the vertical line through 110°F. Then interpolate between these two values in proportion to the absolute humidity. That is, $14.3 + 0.44(15.7 - 14.3) = 14.9$ cu ft per lb of bone-dry air in the example chosen.

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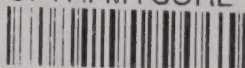
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(A value in parentheses indicates a mass number of the most stable known isotope)

Actinium	Ac	227	Molybdenum	Mo	95.95
Aluminum	Al	26.98	Neodymium	Nd	144.27
Americium	Am			Np	(237)
Antimony	Sb		Acc. No. 3138	Ne	20.183
Argon	A		EX: 62 N54	Ni	58.69
Arsenic	As		WIS (WK).	Nb	92.91
Astatine	At			N	14.008
Barium	Ba			Os	190.2
Berkelium	Bk		trial Sto	O	16.0000
Beryllium	Be		954.	Pd	106.7
Bismuth	Bi			P	30.975
Boron	B			Pt	195.23
Bromine	Br			Pu	(242)
Cadmium	Cd			Po	210
Calcium	Ca			K	39.100
Californium	Cf			Pr	140.92
Carbon	C			Pm	(145)
Cerium	Ce			Pa	231
Cesium	Cs			Ra	226.05
Chlorine	Cl			Rn	222
Chromium	Cr			Re	186.31
Cobalt	Co			Rh	102.91
Copper	Cu			Rb	85.48
Curium	Cm			Ru	101.7
Dysprosium	Dy	162.46	Samarium	Sm	150.43
Erbium	Er	167.2	Scandium	Sc	44.96
Europium	Eu	152.0	Selenium	Se	78.96
Fluorine	F	19.00	Silicon	Si	28.09
Francium	Fr	(223)	Silver	Ag	107.880
Gadolinium	Gd	156.9	Sodium	Na	22.997
Gallium	Ga	69.72	Strontium	Sr	87.63
Germanium	Ge	72.60	Sulfur	S	32.066
Gold	Au	197.2	Tantalum	Ta	180.88
Hafnium	Hf	178.6	Technetium	Tc	(99)
Helium	He	4.003	Tellurium	Te	127.61
Holmium	Ho	164.94	Terbium	Tb	159.2
Hydrogen	H	1.0080	Thallium	Tl	204.39
Indium	In	114.76	Thorium	Th	232.12
Iodine	I	126.91	Thulium	Tm	169.4
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.85	Titanium	Ti	47.90
Krypton	Kr	83.80	Uranium	U	238.07
Lanthanum	La	138.92	Vanadium	V	50.95
Lead	Pb	207.21	Wolfram (tungsten)	W	183.92
Lithium	Li	6.940	Xenon	Xe	131.3
Lutetium	Lu	174.99	Ytterbium	Yb	173.04
Magnesium	Mg	24.32	Yttrium	Y	88.92
Manganese	Mn	54.93	Zinc	Zn	65.38
Mercury	Hg	200.61	Zirconium	Zr	91.22

